







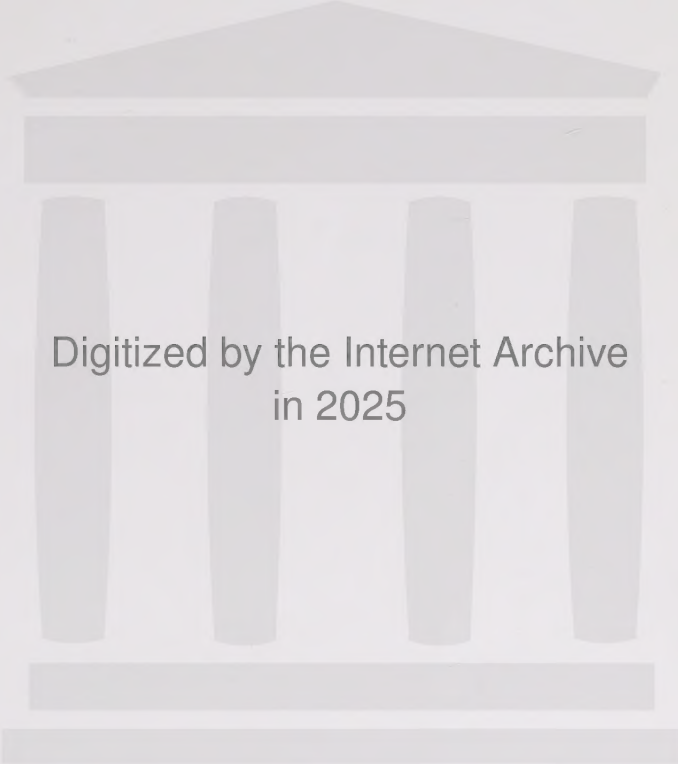
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LECTURES ON  
THEORETICAL PHYSICS



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THE present volume, uniform with Vol. I., contains an almost literal translation of four courses of Professor Lorentz's lectures on Theoretical Physics, viz. *Thermodynamics*, edited in the Dutch language by Mrs. T. C. Clay-Jolles and published in 1921; *Entropy and Probability*, edited by Dr. C. A. Crommelin, published 1923; *The Theory of Radiation*, edited by Dr. A. D. Fokker, published (in a second impression) 1926; and *The Theory of Quanta*, edited by Mrs. G. L. de Haas-Lorentz, published 1919. As in the first volume, only a few minor remarks or explanations, marked by square brackets, were added to the original texts.

L. S.  
A. P. H. T.

ROCHESTER, N.Y.,  
*September 1927.*





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1. The first law of thermodynamics states that the total energy of a closed system is constant. This means that energy cannot be created or destroyed, only transformed from one form to another.

2. The second law of thermodynamics states that the entropy of a closed system always increases over time. Entropy is a measure of the disorder or randomness of a system.

3. The third law of thermodynamics states that the entropy of a perfect crystal at absolute zero is zero.

4. The fourth law of thermodynamics states that the temperature of a system cannot be reached in a finite number of steps.

5. The fifth law of thermodynamics states that the heat capacity of a system is proportional to the square of the temperature.

# THERMODYNAMICS



TO THE  
ASSOCIATION

## THERMODYNAMICS

1. THERMODYNAMICS or the mechanical theory of heat is based upon two laws, the First Law or the Law of Conservation of Energy, and the Second Law.

To begin with, we will consider the first of these laws and will give some brief explanations concerning the fundamental concepts of the theory.

*Quantity of heat.*—Since heat is to be considered as a form of energy, it follows from the conservation law that the internal energy of a body can be increased or diminished in two ways, namely, either by allowing external forces to do positive or negative work upon it, or by supplying or withdrawing heat. Experience teaches us that it is possible in our observations to distinguish these two processes from each other, which does not, however, prevent us from considering them as essentially equal in kind. The exchange of heat should then, even as required by molecular theories, be associated in our thought with the work of forces active between the smallest particles of the bodies which are in contact with each other. We take it for granted that, given a sufficient knowledge of the phenomena, there can be no doubt as to whether we have to do with one or the other type of process, and that it is always possible to deduce from observations the quantity of heat under consideration.

*Internal energy.*—The internal energy of a system depends only upon its instantaneous state and is independent of the process by which the system was brought into this state. It will thus be a function of those magnitudes only which determine the state of the system. In order to express the energy in a given state by a definite number it is necessary to assume some “normal state” for which the energy is taken to be zero. This

state can be chosen arbitrarily. The difference of energies of a system in two states  $A$  and  $B$  will be independent of this choice and will depend only on the states  $A$  and  $B$  themselves. The same thing cannot be said of the quantity of heat supplied to a body during its passage from the state  $A$  to the state  $B$ . For this quantity of heat depends not only on the initial and the final state of the process but also upon the process itself.

*States of equilibrium and reversible processes.*—By a state of equilibrium of a system we mean a state in which it can persist permanently. In such a state all the magnitudes accessible to observation, as *e.g.* the dimensions of the system and the intensity of external forces applied to it, remain constant. Also the internal energy must then be considered as constant.

Again, we can imagine that by a gradual change of the external forces and an appropriate supply or withdrawal of heat a system is made to pass through a series of successive equilibrium states evolving continuously from each other. This is only possible under the condition that the process is an exceedingly slow one. More correctly, we have to consider the limiting case to which the phenomena tend when they take place indefinitely slower and slower. Then only can we disregard the deviations from equilibrium which would be unavoidable for rapid changes.

That a process consisting of a series of states of equilibrium can also take place in the reverse sense, is obvious. Again, if the passage from one state  $A$  to another  $B$  requires a certain heat supply, in the reverse process the same quantity of heat must be taken out.

This follows at once from the energy law by noticing that in the two processes the work of the external forces as well as the change of the internal energy are equal in absolute value but of opposite signs.

Henceforth heat supplied to a system will be reckoned positive and heat given out by the system negative.

2. According to the first law of thermodynamics the heat supplied to a system is equal to the sum of the increase of the internal energy and the work done by the system against external forces. In symbols,

$$Q = \epsilon_2 - \epsilon_1 + A, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $Q$  is the heat given to the system,  $\epsilon$  its internal energy, and  $A$  the work done by the system.

For an infinitesimal change of state,

$$dQ = d\epsilon + dA. \quad (2)$$

Here the meaning of  $d$  in the different terms is not the same. Since  $\epsilon$  is completely determined by the state of the system,  $d\epsilon$  stands for the change of this magnitude  $\epsilon$  and is thus a total differential. On the other hand,  $dQ$  is not the change of a certain magnitude  $Q$ . In fact, a magnitude  $Q$ , a quantity of heat which would be completely determined by the state of the system, does not exist;  $dQ$  is then simply a small quantity of heat given to the system. Such also is the case of  $dA$ ; this again is not the differential of a magnitude  $A$ , but an infinitesimal work done by the system.

The writing down of the above equation is conditioned by the possibility of distinguishing the heat  $Q$  and the work  $A$  from each other in our thoughts and in determining them numerically. The possibility of such a distinction, however, is already implied by what was said at the outset in explanation of the concept of the quantity of heat.

*Work.*—By the work of a force  $K$  we mean the value of the integral  $\int K \cos \theta ds$ , where  $\theta$  is the angle between the direction of the force and the displacement element  $ds$ .

In thermodynamics the case of a uniform normal pressure ( $p$ ), exerted over a surface  $\sigma$ , often occurs. The pressure exerted by the system [body] is equal and opposite to it, so that

$$A = \int \delta \cos \theta p d\sigma = p \int \delta \cos \theta d\sigma = p(v_2 - v_1).$$

Here  $\delta$  is the displacement of the surface element  $d\sigma$  and  $\theta$  the angle between the displacement  $\delta$  and the direction of the pressure  $p$  exerted by the body;  $\int \delta \cos \theta d\sigma$  is then manifestly the increase of volume,  $v_2 - v_1$ . This is still the case when the whole surface or a part of it is displaced *inwards*. Then  $\theta$  is greater than  $90^\circ$  and  $\cos \theta$  negative. For an infinitesimal change of volume we have  $dA = p dv$ , and for a finite expansion with variable pressure  $A = \int p dv$ .

Notice that the same pressure  $p$  prevails also throughout the body only when the process is *reversible*, so that the body is at every instant in a state of equilibrium.



The work done can be represented graphically in a  $pv$ -diagram by the area of the figure contained between the curve expressing the process, the two parallels to the  $p$ -axis through the end-points of this curve, and the  $v$ -axis. In Fig. 1 the area  $ABba$  represents the work.

For a gas obeying Boyle's law and undergoing an isothermal expansion we have

$$A = \int_{v_1}^{v_2} p dv = C \int_{v_1}^{v_2} \frac{dv}{v} = C \log \frac{v_2}{v_1} = p_1 v_1 \log \frac{v_2}{v_1},$$

since  $p_1 v_1 = p_2 v_2 = C$ .

3. Here is another example of calculating the work. Along a string (Fig. 2) transversal vibrations propagate themselves.

Let us lay a dividing plane  $p$  perpendicular to the direction of the stretched string and let us determine

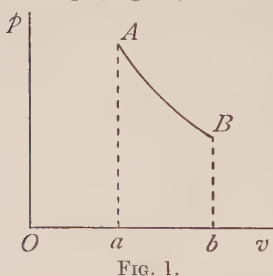


FIG. 1.

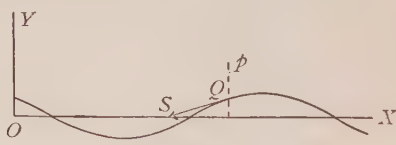


FIG. 2.

the work done by the part of the string on the left of  $p$  upon that on the right of  $p$ .

The displacement may be represented by  $y = a \cos n\left(t - \frac{x}{v}\right)$ , where  $a$  is the amplitude,  $v$  the propagation velocity of the waves, and  $\tau = 2\pi/n$  the period of vibration. The force to be considered is the tension  $S$ , which will be assumed to be constant along the string and also independent of the time, such an approximation being allowed for small displacements. The left-hand part of the string pulls the right-hand one in the direction of  $S$ , that is to say, along the tangent which, of course, changes continually. The point of application of this force is  $Q$ , where the string is cut by the plane  $p$ .

The displacement of  $Q$  during the time  $dt$  is  $\frac{\partial y}{\partial t} dt$ .

The component of  $S$  along the  $y$ -axis is

$$S_y = S \cos (S, y) = -S \sin (S, x),$$

or, since the displacements are assumed to be small,

$$S_y = -S \tan(S, x) = -S \frac{\partial y}{\partial x}.$$

The work done during the time  $dt$  is thus  $-S \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dt$ , and the work per period

$$-S \int_0^T \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dt = \frac{n^2 S a^2}{v} \int_0^{2\pi/n} \sin^2 n \left( t - \frac{x}{v} \right) dt = \frac{\pi n S a^2}{v}.$$

The result is of course positive, since the left part of the string gives up energy to the right part [this being also the direction of propagation]. For vibrations running to the left the work would be negative, since then  $y = a \cos n \left( t + \frac{x}{v} \right)$ .

We may also say that during a vibration period the amount  $\pi n S a^2 / v$  of energy passes from the left-hand to the right-hand part of the string. If, say, a hundred waves are produced, we see, so to speak, the energy carried away by this number of waves. The amount  $\pi n S a^2 / v$  may also be considered as the energy per wave-length.

#### 4. Application to perfect gases.

We will now apply the first law of thermodynamics to a few simple cases, and in the first place to perfect gases. These obey the laws of Boyle and of Guy-Lussac, and their internal energy depends only on the temperature. It is independent of the volume.

A unit of mass being considered, let  $v$  be its volume,  $p$  the pressure, and  $T$  the temperature. Then we can write

$$pv = RT.$$

We take  $v$  and  $T$  as independent variables and consider an infinitesimal change determined by  $dv$  and  $dT$ . For the heat supplied we write  $dQ$ . This is not a differential but simply an infinitesimal quantity of heat.

Now,\*

$$dQ = d\epsilon + p dv = d\epsilon + RT \frac{dv}{v} = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + \left( \frac{\partial \epsilon}{\partial v} \right)_T dv + RT \frac{dv}{v},$$

and since for a perfect gas  $\left( \frac{\partial \epsilon}{\partial v} \right)_T = 0$ ,

\* By subscripts at partial derivatives will be indicated the quantities which are kept constant in the differentiation.

$$dQ = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + RT \frac{dv}{v}. \quad (3)$$

The *specific heat*,  $c$ , is defined as the heat required for raising the temperature by  $1^\circ$ , when derived from an infinitesimal temperature increment. Thus,  $c = \frac{dQ}{dT}$ .

If the volume is constant,

$$dQ = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT,$$

whence  $c_v$ , the specific heat at constant volume,

$$c_v = \left( \frac{\partial \epsilon}{\partial T} \right)_v.$$

If the pressure is constant,  $p dv = R dT$ , and

$$dQ = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + \frac{RT}{v} \frac{R}{p} dT = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + R dT,$$

so that

$$c_p = \left( \frac{\partial \epsilon}{\partial T} \right)_v + R = c_v + R,$$

$c_p$  being the specific heat at constant pressure.

Thus, for a perfect gas,

$$c_p - c_v = R.$$

By means of this relation the mechanical equivalent of heat can be determined. In fact, if the pressure of a gas mass at a given temperature and volume is known,  $R$  and therefore also  $c_p - c_v$  can be determined in work units, while  $c_p$  and  $c_v$  can be measured calorimetrically, in heat units.

The specific heat of a gas as determined in the usual way, viz. by allowing the gas to flow from a reservoir at a higher temperature through a spiral tube placed in a calorimeter, is  $c_p$ .

The volume of the flowing gas is not constant, but neither is the pressure, for the flow is just due to a pressure difference.

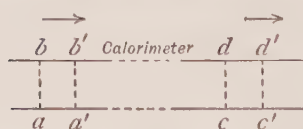


FIG. 3.

Let us fix our attention upon a gas mass contained between  $ab$  and  $cd$  (Fig. 3) and let us follow it on its way until it comes to occupy, say, the space between  $a'b'$  and  $c'd'$ .

Further, let us make the simplifying assumption that the state is stationary, so that the calorimeter gains as much heat as it radiates. The latter

amount of heat can be determined. Under these conditions let us apply the first law.

The increase of internal energy will be equal to the difference in internal energy of the gas mass contained in the space  $cdc'd'$  and that within  $abb'a'$ . Both of these volumes must contain the same mass of gas, which we will denote by  $m$ . Let the state within  $aa'b'b$  be determined by  $p_1, T_1, v_1, \epsilon_1$ , the last two magnitudes being taken per mass unit, and the state within  $cc'd'd$  by  $p_2, T_2, v_2, \epsilon_2$ .

Then

$$\Delta\epsilon = m(\epsilon_2 - \epsilon_1)$$

and

$$A = m(p_2v_2 - p_1v_1),$$

and therefore,

$$Q = m\{(\epsilon_2 - \epsilon_1) + (p_2v_2 - p_1v_1)\} = m\{(\epsilon_2 - \epsilon_1) + R(T_2 - T_1)\}.$$

Thus the determined specific heat is

$$\frac{Q}{m(T_2 - T_1)} = \frac{\epsilon_2 - \epsilon_1}{T_2 - T_1} + R = c_v + R = c_p.$$

Only for a small change can we write  $\frac{\epsilon_2 - \epsilon_1}{T_2 - T_1} = c_v$ . In

general  $(\epsilon_2 - \epsilon_1)/(T_2 - T_1)$  will be the mean value of  $c_v$  taken over the temperature interval; the experiment gives then the mean value of  $c_p$ .

We have here disregarded the kinetic energy of the gas stream. Its increase is  $\frac{1}{2}m(u_2^2 - u_1^2)$ , if  $u_1$  and  $u_2$  be the velocities in  $aa'b'b$  and  $cc'd'd$ . This difference, however, can be neglected.

5. Let us still consider the stationary flow of a fluid through a tube of variable width (Fig. 4). The temperature at different cross-sections may be different, but stationary, and at certain parts of the tube heat may be supplied or taken out. There are no other external forces than the pressure.\*

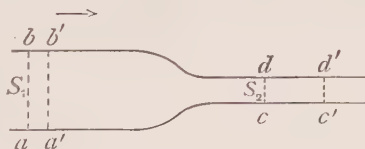


FIG. 4.

As in the preceding case let us consider the fluid within the space  $acdb$  and let us apply to it the first law. Let  $S_1$  and  $S_2$  be the cross-sections,  $u_1$  and

\* Notice, for this and the preceding case, that if the walls of the tube are included in the system the friction at these walls belongs to the inner forces, which needs scarcely to be mentioned.

$u_2$  the velocities, and  $\rho_1$  and  $\rho_2$  the densities at  $ab$  and  $cd$  respectively. After a time  $dt$  this mass of fluid will occupy the space  $a'c'd'b'$ , say. The work done during this time by the external forces will be  $(p_1S_1u_1 - p_2S_2u_2)dt$ .

Thus, if  $qdt$  be the heat supplied during this time,

$$(p_1S_1u_1 - p_2S_2u_2 + q)dt$$

will be equal to the increase of energy of the displaced amount of fluid and thus also to the difference in energy of the fluid within the spaces  $cc'd'd$  and  $aa'b'b$ . Now, the mass contained in each of these is  $\rho_2S_2u_2dt = \rho_1S_1u_1dt$ , and therefore, the difference in kinetic energy of mass-motion,  $\frac{1}{2}\rho_2S_2u_2dt(u_2^2 - u_1^2)$ . Whence, after division by  $dt$ , the required equation,

$$p_1S_1u_1 - p_2S_2u_2 + q = \frac{1}{2}\rho_2u_2S_2(u_2^2 - u_1^2) + \rho_2u_2S_2(\epsilon_2 - \epsilon_1),$$

or, dividing by  $\rho_1S_1u_1 = \rho_2S_2u_2$ ,

$$\frac{p_1}{\rho_1} - \frac{p_2}{\rho_2} + q' = \frac{1}{2}(u_2^2 - u_1^2) + \epsilon_2 - \epsilon_1.$$

Here  $\epsilon_1$ , and similarly  $\epsilon_2$ , is the internal energy which together with the kinetic energy of the mass-motion makes up the total energy, and  $q'$  is the quantity of heat supplied during the passage of a mass unit.

This equation is to be applied to the common case of fluids flowing through a tube. We may also return from it to the preceding case, the determination of  $c_p$  for gases, in which we have neglected the term  $u_2^2 - u_1^2$ .

The famous experiment of Kelvin and Joule, with a tube divided by a porous plug, is again a special case of that just considered. The gas flows through the plug, under a considerable pressure difference, in a stationary stream. During the experiment the pressure in front of and behind the plug remains constant. We have to find the relation of the temperatures on either side of the plug under the assumption that the flow takes place adiabatically. The term  $u_2^2 - u_1^2$  can again be neglected.

Thus, and since  $1/\rho$  is the specific volume  $v$ , the equation becomes

$$p_1v_1 - p_2v_2 = \epsilon_2 - \epsilon_1. \quad . \quad . \quad . \quad . \quad (4)$$



If we have to do with a perfect gas,  $\epsilon$  depends on the temperature only, and we can write

$$\begin{aligned} p_1 v_1 - p_2 v_2 &= c_v (T_2 - T_1) \\ \text{or} \quad -R(T_2 - T_1) &= c_v (T_2 - T_1), \end{aligned}$$

whence it follows that

$$T_1 = T_2.$$

If the gas is not perfect, there is a temperature difference (Joule-Kelvin effect) which can be deduced from equation (4) by further energy considerations. *Vice versa*, from the observed temperature difference conclusions can be drawn by means of (4) about the energy in different states of the gas. For a non-perfect gas the energy is a function not only of the temperature but also of the volume.

6. Let us once more consider any homogeneous body. Between the three magnitudes  $p$ ,  $v$ , and  $T$  determining its state there is a relation called the equation of state. Two only of these three magnitudes can, therefore, be considered as independent variables.

With  $v$  and  $T$  as independent variables the first law becomes

$$dQ = \left( \frac{\partial \epsilon}{\partial v} \right)_T dv + \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + p dv. \quad . \quad . \quad . \quad (5)$$

From the work done, which is the product of the pressure and the increase of volume, and from the heat  $dQ$  supplied, the energy increase can thus be found. For liquids and for solid bodies the work can often be neglected. Thus, for instance, in the case of melting, the energy difference between the liquid and the solid phase, both taken at the melting temperature, is known directly from the heat of melting. Let us apply this to the following case :

A vessel contains water at  $-a^\circ$ , which is brought suddenly to a partial freezing (*e.g.* by throwing into it a small crystal of ice). What part of the water will freeze? Since no heat is being supplied and since the work done can be disregarded, the energy of the system remains constant, while the temperature mounts to  $0^\circ$ . Suppose we have 1 kg. of water, of which  $x$  kg. freezes. Let  $\epsilon_2$  be the energy of a mass unit of water at  $-a^\circ$ ,  $\epsilon_1$  that at  $0^\circ$ , and  $\epsilon_3$  the energy of a mass unit of ice at  $0^\circ$ . Then

$$\epsilon_2 = (1 - x)\epsilon_1 + x\epsilon_3,$$

and therefore,

$$x = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 - \epsilon_3} = \frac{ac}{r},$$

where  $c$  is the mean specific heat of water between  $-a^\circ$  and  $0^\circ$  ( $c$  is approximately  $= 1$ ) and  $r$  the heat of melting. If  $a$  is greater than  $r/c$ , this would give  $x > 1$  [which is absurd]. The explanation is that in this case not only would the whole water freeze but the final temperature of the ice would still lie below  $0^\circ$ .

In the case of evaporation the external work cannot be disregarded. Suppose that a unit mass of liquid is under the pressure of its saturated vapour and that it begins to evaporate while the temperature is left constant. Let  $v_1$  be the specific volume of the liquid,  $v_2$  that of the vapour,  $r$  the heat of evaporation,  $p$  the pressure,  $\epsilon_1$  the internal energy of the liquid, and  $\epsilon_2$  that of the vapour. Then, by the first law,

$$r = \epsilon_2 - \epsilon_1 + p(v_2 - v_1),$$

whence

$$\epsilon_2 = \epsilon_1 + r - p(v_2 - v_1). \quad . \quad . \quad . \quad . \quad (6)$$

This holds good for every temperature, and since  $\epsilon_1$  is known for all temperatures,  $\epsilon_2$  will be found as a function of temperature. At the same time the so-called specific heat of saturated vapour, which we will denote by  $h$ , can be determined. This is defined as the quantity of heat which must be supplied to a mass unit of saturated vapour in order to raise its temperature by  $1^\circ$ , while its volume is so regulated that the vapour remains just saturated.

In the first place, we have

$$hdT = d\epsilon_2 + pdv_2.$$

Differentiating (6) with respect to  $T$ , that is to say, applying that equation to two temperatures slightly differing from each other, we find

$$\frac{d\epsilon_2}{dT} = \frac{d\epsilon_1}{dT} + \frac{dr}{dT} - p\frac{dv_2}{dT} + p\frac{dv_1}{dT} - (v_2 - v_1)\frac{dp}{dT},$$

so that

$$h = \frac{d\epsilon_2}{dT} + p\frac{dv_2}{dT} = \frac{d\epsilon_1}{dT} + \frac{dr}{dT} + p\frac{dv_1}{dT} - (v_2 - v_1)\frac{dp}{dT}.$$

Since the specific heat of the liquid is

$$c = \frac{d\epsilon_1}{dT} + p \frac{dv_1}{dT},$$

the last expression becomes

$$h = c + \frac{dr}{dT} - (v_2 - v_1) \frac{dp}{dT}.$$

Here  $c$  stands, rigorously, for the specific heat of the liquid under the pressure of the saturated vapour, but may without perceptible error be replaced by the specific heat at constant pressure.

Clausius speaks of the specific heat of saturated vapour already in his first paper, of 1857. His investigations have led to beautiful experimental confirmations.

For steam Clausius found from measurements of  $r$  and  $p$  the formula

$$h = 1.013 - \frac{800.3}{273 + t}.$$

The value of  $h$  is negative, except for temperatures which are very close to the critical temperature (for water  $365^\circ$  C.). Thus, to obtain saturated steam of higher temperature by compression, heat must be taken out. If saturated steam is compressed adiabatically, it becomes unsaturated. In adiabatic expansion it is liquefied.

For carbon disulphide  $h$  is again negative, for ethyl ether positive, for chloroform up to  $120^\circ$  negative, and above this temperature positive. Thus, if saturated vapour of ethyl ether is allowed to expand adiabatically, it becomes unsaturated, and if it is compressed adiabatically, a cloud will be formed. This was beautifully confirmed by Hirn's and later by Cazin's experiments.

7. To conclude this list of examples, let us still consider an application to chemistry, viz. to the variation of the heat of reaction with the temperature. Let  $A$  be a system, composed of several substances, which can transform itself into another system  $B$ . The reaction can take place at different temperatures. The pressure will be assumed to remain constant.

Suppose that the heat supply  $Q$  necessary for the transformation of the system  $A$  into the system  $B$  at the temperature  $t$  is known, as well as the quantities of heat required to raise

the temperature of  $A$  and of  $B$  from  $t$  to  $t + dt$ , for which quantities we may write  $c_A dt$  and  $c_B dt$ , if  $c_A$  and  $c_B$  be the specific heats of the systems  $A$  and  $B$ . From these data we have to deduce the heat supply  $Q'$  necessary for the transformation of the system  $A$  into the system  $B$  at the temperature  $t + dt$ . Since the pressure is supposed to remain unaltered, the total heat supply in the transformation of  $A$  into  $B$  will be the same, whether the process takes place at the temperature  $t$ , or  $A$  is first heated up to  $t + dt$ , then transformed into  $B$  at the temperature  $t + dt$ , and  $B$  is cooled down to the temperature  $t$ .

Thus we can write

$$Q = c_A dt + Q' - c_B dt$$

or also

$$\frac{Q' - Q}{dt} = c_B - c_A.$$

The temperature coefficient of the heat supply  $Q$  necessary for the transformation of  $A$  into  $B$  is thus determined by the difference of the specific heats of the systems  $A$  and  $B$ . In the inverse reaction, transforming  $B$  into  $A$ , the quantity of heat  $Q$  will be generated.

#### 8. The Second Law of Thermodynamics.

Clausius' principle may be stated as follows :

In a system of bodies no such changes are possible at the end of which, while all remaining bodies have returned to their initial state, two of them should assume a state which might also be obtained by a transfer of heat from that at lower to that at higher temperature. More briefly, a mere transfer of heat from a colder to a hotter body, unaccompanied by some other processes, is not possible.

With regard to the definition of " temperature " the following remark may be made.

Experiment teaches us that all bodies can be arranged into an ascending series such that a higher placed body will always give up heat to one placed lower. The higher placed body is then said to have a higher temperature. Two bodies which do not give up heat to each other will occupy the same place in the series and will be given the same temperature.

In order to draw conclusions from Clausius' principle, we have to use " cycles ", *i.e.* changes carrying the body or system back to its original state.

We have, further, to bear in mind the distinction between reversible and irreversible changes. What is meant by a reversible change was already explained on p. 4.

9. What is known as Carnot's cycle is a closed process consisting of two isothermal and two adiabatic reversible changes. A graphical representation of such a cycle in the  $p$ - $v$ -diagram, for an ideal gas as working body, is given in Fig. 5, where  $AB$  and  $CD$  are isothermals. The corresponding temperatures are  $T_1$  and  $T_2$ , and it will always be assumed that  $T_1 > T_2$ .  $AD$  and  $BC$  are adiabatics.

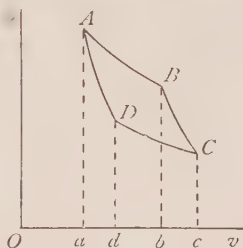


FIG. 5.

For the isothermal process  $AB$  a heat reservoir  $R_1$  of temperature  $T_1$  is required, which supplies to the working body a quantity of heat  $Q_1$ . We suppose this reservoir to have a great capacity, so that its temperature is not decreased by the giving up of heat. During the process  $CD$  a quantity of heat  $Q_2$  is given up to another, similar heat reservoir  $R_2$  of temperature  $T_2$ . During the changes  $BC$  and  $DA$  there is no heat transfer. Thus the area  $ABCD$  will correspond to  $Q_1 - Q_2$ . In fact,  $ABCD$  represents the work  $A$  done by the working substance in the whole cycle, and this is equal to the total heat supplied to the substance, since its internal energy returns after the completion of the cycle to its original value.

If the process is reversed,  $R_2$  gives up the quantity of heat  $Q_2$ , which is transferred to  $R_1$ ; in addition, the external forces do work upon the substance (to the amount  $A$ ) and this is transformed into heat which is also given up to  $R_1$ , so that this reservoir receives in all the quantity of heat  $Q_1 = Q_2 + A$ .

We can imagine that the reservoirs are brought into contact with the working substance automatically at the right moment.

In this way a hot-air motor could be constructed by connecting the piston of the gas cylinder with the axle of a fly-wheel. If the machine is run in the reverse sense, heat will pass from the colder to the hotter reservoir, an equivalent amount of external work being done upon the gas.

Similarly, other systems can be taken through a Carnot cycle of changes, as *e.g.* a liquid, or a system composed partly



of water and partly of steam, etc. The process for the last-mentioned case is represented by the  $pv$ -diagram in Fig. 6, assuming that the piston is never allowed to rise so high that the whole water should evaporate. The isotherms are straight

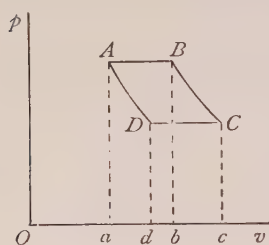


FIG. 6.

lines parallel to  $OV$ , since, when liquid and vapour are in contact, the pressure has at a given temperature a determined value.

10. The first important conclusion about the Carnot cycle is, that the ratio of the quantities of heat  $Q_1$  and  $Q_2$  is independent of the nature of the working substance and depends only upon the temperatures of the reservoirs. The ratio of the work done by the substance to the heat given up by  $R_1$ , *i.e.*  $Q_1 - Q_2/Q_1$ , being called the efficiency, we may say briefly that the efficiency of a Carnot cycle is independent of the nature of the working substance. To prove this, let us suppose that the efficiency is  $n$  for one, and  $n'$  for another working substance. Then the first substance will, out of  $nA$  units of heat taken from  $R_1$ , use up  $A$  units for mechanical work. Let us now make the second engine work backwards, driving it by the first. When the first does upon the second an amount of work equivalent to  $A$  heat units, the second engine carries back to  $R_1$  the quantity of heat  $n'A$ . Now, if  $n'$  were greater than  $n$ , the reservoir  $R_1$  would have gained  $(n' - n)A$  heat units and  $R_2$  would have lost as many, while the working substances, having completed their cycles, would have returned to their initial state, so that ultimately, against Clausius' principle, heat would be transferred from the colder body  $R_2$  to the hotter  $R_1$  without any change in the remaining bodies. Thus  $n'$  cannot be greater than  $n$ . Similarly, exchanging the rôles of the two engines, *i.e.* allowing the first engine to be driven by the second, the former completing a reverse or negative and the second a positive Carnot cycle, it will be seen that  $n'$  cannot be smaller than  $n$ . Thus the only possibility left is  $n' = n$ , which was to be proved.

We can write, therefore,

$$\frac{Q_1}{Q_2} = f(T_1, T_2).$$

The form of this function can be determined in two ways.

First, we may agree to measure the temperature by means of a gas thermometer, filled with an ideal gas. This amounts to making the temperature proportional to the product  $pv$ , in accordance with the law of Boyle and Gay-Lussac,  $pv = RT$ .

Let us, then, allow the ideal gas to complete a Carnot cycle and let us find the corresponding value of  $Q_1/Q_2$ . Since the value of  $Q_1/Q_2$  is independent of the nature of the working substance, we know that the result will have general validity.

The area of the figure  $abBA$  (Fig. 7) represents the work done by the gas in the isothermic process  $AB$ , and that of the figure  $dcCD$  the work done upon the gas in the isothermal process  $CD$ . The internal energy, which for an ideal gas depends only on the temperature, does not change during either isothermic process. By the first law, therefore, the area of  $abBA$  will represent the heat  $Q_1$  and similarly  $dcCD$  the heat  $Q_2$ . The difference of these areas will represent the value of  $Q_1 - Q_2$ . But  $Q_1 - Q_2$  is also represented by the area  $ABCD$ . This is possible only when the area  $Aadd$  is equal to the area  $Bbcc$ .

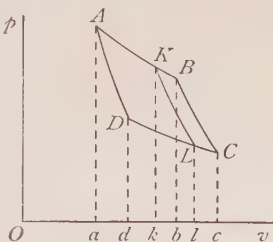


FIG. 7.

Thus the work done during the adiabatic changes  $AD$  and  $BC$  is the same. This could also be seen directly, remembering that for the adiabatics the work done is equal to the decrease of internal energy which depends only on the temperature and is thus here the same for both adiabatics.

Turning to the determination of  $Q_1/Q_2$ , let us start from the equation, valid for a small adiabatic change,

$$0 = pdv + \epsilon'(T)dT,$$

where the last term represents the change of the internal energy corresponding to the temperature variation  $dT$ .

Since  $pv = RT$ , this becomes

$$0 = RT \frac{dv}{v} + \epsilon'(T)dT,$$

the differential equation of the adiabatic lines. Thus, by integration,

$$\log v + \frac{1}{R} \int \epsilon'(T) \frac{dT}{T} = \text{const.},$$

and if this be applied to the expansion from  $v_1$  to  $v_2$ ,

$$\log \frac{v_2}{v_1} + \frac{1}{R} \int_{T_1}^{T_2} \epsilon'(T) \frac{dT}{T} = 0.$$

Whence we see that an adiabatic temperature variation, between given temperature limits, is always accompanied by a change of volume in a determined ratio.

For every point  $K$  on  $AB$  (Fig. 7) a point  $L$  on  $DC$  can be determined, such that  $K$  and  $L$  are on the same adiabatic.

Thus  $\frac{Ol}{Ok} = q$ , where  $q$  depends on  $T_1$  and  $T_2$  alone.

Again, by the law of Boyle and Gay-Lussac,

$$(Ol \times lL) : (Ok \times kK) = T_2 : T_1,$$

and therefore,

$$Ll : Kk = T_2 : qT_1,$$

so that also the ratio of pressures at two points of an adiabatic depends on the temperatures only. Consequently, the figures  $aABb$  and  $dDCc$ , whose areas represent  $Q_1$  and  $Q_2$ , can be obtained from each other by dilatation and contraction along the axes. To pass from the former to the latter, the dimensions in the direction  $Op$  have to be altered in the ratio of 1 to  $q$ , and those in the direction  $Ol$  in the ratio of  $qT_1$  to  $T_2$ . For the ratio of the areas, *i.e.* for  $Q_1/Q_2$ , we thus find  $\frac{1}{q} \cdot \frac{qT_1}{T_2} = \frac{T_1}{T_2}$ , which is the required temperature function.

Thus our result is

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Here  $T_1$  and  $T_2$  are the temperatures as measured by an ideal-gas thermometer, *i.e.* the absolute temperatures determined by the law,  $pv = RT$ , of ideal gases.

11. The alternative way of obtaining the required temperature function is as follows.

The absolute temperature is simply defined by giving to

the ratio  $Q_1/Q_2$  the value  $T_1/T_2$ , that is to say, in order to find the ratio of the temperatures of two bodies 1 and 2, we subject an arbitrary working substance to a Carnot cycle, in which the bodies 1 and 2 serve as heat reservoirs, and determine for this cycle the ratio of the quantities of heat  $Q_1$  and  $Q_2$ . And since the absolute numerical values of all temperatures are known, if a given number is assumed for the difference of two arbitrarily chosen temperatures (as *e.g.* 100 for the difference between the boiling point of water and the melting point of ice), the absolute temperature is therewith completely fixed. In virtue of its definition it is always positive.

The absolute temperature thus defined must have the property that, if first a Carnot cycle is carried out between the temperatures  $t_1$  and  $t_2$  (on an arbitrary scale), followed by another between  $t_2$  and  $t_3$ , so that the reservoir  $R_2$  of temperature  $t_2$  on the whole neither receives nor gives up heat, and then a Carnot cycle is carried out directly between  $t_1$  and  $t_3$ , the same value should be found in both cases for the ratio of the absolute temperatures corresponding to  $t_1$  and  $t_3$ . Such, in fact, is the case.

For, let in the cycle between  $R_1$  (temp.  $t_1$ ) and  $R_2$  (temp.  $t_2$ ) the quantity of heat  $Q_1$  be taken from  $R_1$  and the quantity  $Q_1/f(t_1, t_2)$  given to  $R_2$ . Then, by what has just been said, in the cycle between  $R_2$  and  $R_3$  the quantity of heat  $Q_1/f(t_1, t_2)$  must be taken from  $R_2$ , so that  $R_3$  will receive the heat  $Q_1/f(t_1, t_2)f(t_2, t_3)$ , while in the direct cycle between  $R_1$  and  $R_3$  the latter receives  $Q_1/f(t_1, t_3)$ . Thus we must have

$$f(t_1, t_3) = f(t_1, t_2)f(t_2, t_3).$$

This condition is indeed satisfied if we put

$$f(t_1, t_2) = \frac{T_1}{T_2}.$$

12. The formula  $Q_1/Q_2 = T_1/T_2$ , which holds good for a Carnot cycle, can be written

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

or also

$$\sum \frac{Q}{T} = 0, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the left-hand member being the algebraic sum of the quantities of heat supplied, each divided by the corresponding temperature.

Let us now consider any reversible cycle. The temperature will then, in general, vary continually. If the whole process is subdivided into infinitesimal steps and if  $dQ$  be the heat supplied in any one of these steps to the working substance, then,

$$\int \frac{dQ}{T} = 0, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which can be considered as a generalisation of the equation (8).

We will prove this first for a working substance whose state is determined by its volume and pressure ( $v, p$ ). The cycle being represented by a closed curve  $L$  (Fig. 8), we subdivide it by adiabatics  $ab, lc$ , etc., and isothermals  $ad, bc$ , etc., into infinitesimal Carnot cycles, such as  $adcb$ , etc. The outermost triangular figures will be infinitely small, of higher order, and can thus be neglected.

Now, let  $dQ_{ad}$  be the heat supplied in the step  $ad$ , and  $dQ_{bc}$  in  $bc$ , the order of the suffixes indicating the sense of the process. Then

$$dQ_{ad} : dQ_{bc} = T_a : T_b, \text{ and } dQ_{cb} = -dQ_{bc},$$

so that

$$\frac{dQ_{ad}}{T_a} + \frac{dQ_{cb}}{T_b} = 0,$$

and if all such items are added up, we have  $\int \frac{dQ}{T} = 0$ , where the

integration is extended over the given closed curve. In fact,  $dQ_{ad}$  can be replaced by  $dQ_{al}$ ; for, since  $dQ_{ld} = 0$ ,  $dQ_{al} + dQ_{da}$  or  $dQ_{al} - dQ_{ad}$  is the work done in the cycle  $adl$  which is represented by the area  $adl$  and is therefore infinitesimal of the second order.

13. In the next place we will give a general proof of the equation  $\int \frac{dQ}{T} = 0$  for a reversible cycle  $K$ .

For this purpose we consider a perfectly arbitrary cycle of changes which will be subdivided into infinitesimal steps. We suppose that at every instant the temperature of all parts of the system is the same. In each step an infinitesimal quantity of heat  $dQ$ , which may be positive or negative, will be taken up

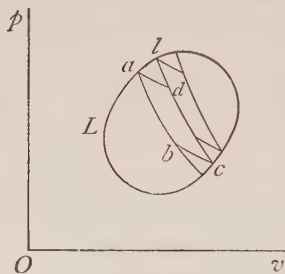


FIG. 8.



by the system at the instantaneous temperature  $T$ . Now, let us suppose that each of these quantities  $dQ$  is taken by means of a Carnot cycle from a single heat reservoir  $R$  of temperature  $\theta$  and of so great capacity that during the process  $\theta$  remains constant. Let, moreover, in each of these auxiliary cycles  $R$  be one and the system or body undergoing the cycle  $K$  the other heat reservoir. Then, by (7), the quantity of heat taken from  $R$  in one of the steps is  $\theta \frac{dQ}{T}$  and, for the whole process,

$$\theta \int \frac{dQ}{T}.$$

Now, this expression cannot be positive; for, since the system which has gone through the cycle as well as all the bodies which were used for the auxiliary cycles have returned to their original state, the heat taken from  $R$  would then be entirely transformed into work. This, however, is, by Kelvin's principle, impossible.

Kelvin's principle says: It is impossible that the only result of a series of changes undergone by a system of bodies should consist in taking from a body  $A$  a certain quantity of heat  $w$  and transforming it entirely into work. This principle is closely connected with that of Clausius (p. 14). In fact, if a quantity of heat  $w$  could be entirely transformed into work, this work could be used in a reverse Carnot cycle, with the body  $A$  as the reservoir of higher temperature, in order not only to return to  $A$  the heat  $w$ , but to give it in addition a quantity of heat taken from a reservoir  $B$  of lower temperature. The net result would then be a mere transfer of heat from  $B$  to  $A$ , which is against Clausius' principle.

Thus the expression  $\theta \int \frac{dQ}{T}$ , and therefore also  $\int \frac{dQ}{T}$ , cannot be positive. There would remain only  $\int \frac{dQ}{T} \leq 0$ . But since the process is reversible,  $\int \frac{dQ}{T} < 0$  for this process would entail  $\int \frac{dQ}{T} > 0$  for the reverse process, which is again impossible. Consequently, the only possibility left for a reversible process is

$$\int \frac{dQ}{T} = 0.$$

In words: the sum of the reduced quantities of heat is zero, if "reduced" stands for "divided by the absolute temperature".

14. Suppose now that we can pass from a state  $A$  to a state  $B$  by different reversible paths. Then

$$\int_A^B \frac{dQ}{T}$$

must have for each of these paths the same value. In fact, passing from  $A$  to  $B$  along a path  $L_1$  and back from  $B$  to  $A$  along  $L_2$ , we complete a cycle, for which the total value of  $\int \frac{dQ}{T}$  is nil. The values of the integral for the passage from  $A$  to  $B$  and the return are, therefore, equal and of opposite signs. But since the path  $L_2$  as well as  $L_1$  is reversible, we can also pass along  $L_2$  from  $A$  to  $B$ , and  $\int_A^B \frac{dQ}{T}$  will then have the same value as along  $L_1$ .

Let us now choose a state  $N$  with which all other states of the system can be compared.\* Then, if  $A$  be any of these states, we can imagine the system carried along a reversible path from  $A$  to  $N$ . To this passage will correspond a determined value of  $\int \frac{dQ}{T}$  which, as was just proved, is independent of the path chosen and thus, the state  $N$  being chosen once and for all, depends only on the state  $A$ . This value of the integral is termed *the entropy* of the system in the state  $A$ .

The entropy will always be denoted by  $\eta$ .

The value of  $\int \frac{dQ}{T}$  for a reversible transition from a state  $A$  to a state  $B$  is readily seen to be equal to the increase of entropy in this transition. For, the integral being independent of the path chosen, the system may first be brought into the state  $N$  and thence into  $B$ . The required integral will then become

$$\int_A^B \frac{dQ}{T} = \int_A^N \frac{dQ}{T} + \int_N^B \frac{dQ}{T} = \eta_B - \eta_A, \quad (10)$$

since, by definition,

$$\int_N^B \frac{dQ}{T} = \eta_B, \quad \int_A^N \frac{dQ}{T} = \eta_A, \quad \text{and therefore, } \int_A^B \frac{dQ}{T} = \eta_B - \eta_A.$$

\* Cf. the remarks made about energy on p. 3.

Rigorously, the given definition of entropy holds only for states of equilibrium, for these only can be reached by reversible changes. There are cases, however, in which though there be no equilibrium, we can speak of entropy. Such, *e.g.*, is the case of water in presence of steam which has not attained its maximum tension. If we imagine them divided by a membrane, each phase separately can remain in equilibrium and we may then speak of the sum of their entropies.

If the two states *A* and *B* differ from each other infinitesimally, formula (10) becomes

$$\frac{dQ}{T} = d\eta. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Thus, if  $dQ$  is the heat taken up from outside by a body in its passage from one state of equilibrium to another infinitely near one,  $dQ/T$  is a total differential.

In this form the Second Law has found many applications. Having introduced convenient variables, whose values characterise a state of equilibrium, one can express  $dQ$  in terms of the differentials of these variables and make use of the relations which must hold between the coefficients of  $dQ/T$  in order that this magnitude should be a total differential. As to  $dQ$  itself, this is obtained in accordance with the First Law by writing down the heat supplied as the sum of the increase of the internal energy and of the work done by the system.

That  $dQ/T$  is a total differential, follows by the preceding considerations from the fact that  $\int \frac{dQ}{T}$  vanishes for a reversible cycle. *Vice versa*, if we know that  $dQ/T$  is a differential of a certain magnitude,\* we can conclude that  $\int \frac{dQ}{T} = 0$  for any reversible cycle.

The magnitude  $dQ$  itself is not a differential but represents only an infinitesimal quantity of heat. For a cycle  $\int dQ$  is not zero but equal to the work done.

The temperature  $T$  is an integrating divisor of the expression  $dQ$ . There are, of course, infinitely many integrating divisors, and the remarkable thing is that one of them can play the rôle of temperature, of a magnitude, that is, which decides whether

\* [One-valued function of the state.]

heat will pass from one body to another. But not all integrating divisors have this physical significance. If for a certain body  $dQ/D_1$ , say, is a total differential, where  $D_1$  is some function of the variables determining the state of the body, and  $D_2$  a similar function for another body, then, if these bodies are in equilibrium with each other,  $D_1$  need not in general be equal to  $D_2$ .\*

15. We will now consider some simple applications.

Let a body of uniform temperature  $T$  and volume  $v$  be subjected to a pressure  $p$ , normal to its surface. Between  $p$ ,  $v$ , and  $T$  there is a relation. This applies to gases, liquids, and solids which are subjected to such a pressure only.

Let our independent variables be  $v$  and  $T$ .

Then, by the first law,

$$dQ = \left(\frac{\partial \epsilon}{\partial T}\right)_v dT + \left(\frac{\partial \epsilon}{\partial v}\right)_T dv + p dv,$$

whence 
$$\frac{dQ}{T} = \frac{1}{T} \left(\frac{\partial \epsilon}{\partial T}\right)_v dT + \frac{1}{T} \left\{ \left(\frac{\partial \epsilon}{\partial v}\right)_T + p \right\} dv.$$

Since this is a total differential, we must have

$$\frac{\partial}{\partial v} \left\{ \frac{1}{T} \left(\frac{\partial \epsilon}{\partial T}\right)_v \right\} = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[ \left(\frac{\partial \epsilon}{\partial v}\right)_T + p \right] \right\}$$

or 
$$\frac{1}{T} \frac{\partial^2 \epsilon}{\partial v \partial T} = - \frac{1}{T^2} \left\{ \left(\frac{\partial \epsilon}{\partial v}\right)_T + p \right\} + \frac{1}{T} \left( \frac{\partial^2 \epsilon}{\partial T \partial v} + \frac{\partial p}{\partial T} \right),$$

or also 
$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p. \quad . \quad . \quad . \quad . \quad (12)$$

The right-hand member can be determined experimentally. The second law shows us, therefore, how the internal energy depends on volume.

For a *perfect* gas  $pv = RT$ , so that

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

and 
$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = \frac{RT}{v} - p = 0.$$

We thus see that the internal energy is independent of volume. This is exactly the second characteristic we have

\* From (11) follows that  $T$  is not the only integrating divisor of  $dQ$ , and that  $f(\eta)T$ , where  $f(\eta)$  is an arbitrary function of the entropy, has the same property. Now, it is obvious that if the temperatures of two bodies are equal, such arbitrarily chosen integrating divisors need not be equal.

assumed for an ideal gas (cf. p. 7), its first characteristic being the validity of the law  $p v = R T$ .

The second law of thermodynamics connects these two properties with each other; for, *vice versa*, it follows also from

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = 0 \text{ that}$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = 0,$$

and therefore,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{p}{T}, \quad \frac{dp}{p} = \frac{dT}{T},$$

$$\log p = \log T + \log C$$

or

$$p = C T.$$

For an infinitesimal adiabatic change

$$\left(\frac{\partial \epsilon}{\partial T}\right)_v dT + p dv = 0,$$

i.e. the decrease of the internal energy is equal to the work done by the gas.

For a finite change the differential equation has to be integrated. This equation can be written

$$c_v \frac{dT}{T} + \frac{R}{v} dv = 0.$$

Thus, by integration, if the specific heat  $c_v$  be considered as a constant,

$$c_v \log T + R \log v = C,$$

$$c_v \log T + (c_p - c_v) \log v = C,$$

$$\log T + (k - 1) \log v = C, \text{ where } \frac{c_p}{c_v} = k,$$

or ultimately,

$$T v^{k-1} = C = T_0 v_0^{k-1}. \quad . \quad . \quad . \quad (13)$$

If between this equation and  $p v = R T$  the temperature be eliminated, we find

$$p v^k = \text{constant} = p_0 v_0^k, \quad . \quad . \quad . \quad (14)$$

and if the volume be eliminated,

$$T^k p^{1-k} = \text{constant} = T_0^k p_0^{1-k}$$

or

$$\frac{1}{T} p^{1-\frac{1}{k}} = \text{constant}. \quad . \quad . \quad . \quad (15)$$



The formulae (13), (14), and (15) are due to Poisson. They hold good for reversible adiabatic changes of ideal gases.

16. The value of  $k$  can be determined by adiabatic experiments. A globe is filled with a gas at a pressure  $p_1$  higher than the atmospheric pressure  $p_0$ , and at the temperature  $T$  of the environment. The globe is connected to a tube with a wide-bore tap. The tap being turned on, the gas expands rapidly, and therefore adiabatically down to the pressure  $p_0$ . Its temperature falls to  $T'$ . As soon as the gas has thus expanded, the tap is turned off again. The temperature of the gas in the globe returns then after a certain time to its original value  $T$ , while its pressure mounts to  $p_2$ ;  $p_1 > p_2 > p_0$ .

The last change takes place at a constant volume, so that

$$\frac{p_0}{T'} = \frac{p_2}{T} \text{ or } T' = T \frac{p_0}{p_2}.$$

The first change being adiabatic, let us apply to it Poisson's formula. Then

$$\frac{p_1^{1-\frac{1}{k}}}{T} = \frac{p_0^{1-\frac{1}{k}}}{T'} = \frac{p_0^{-\frac{1}{k}} p_2}{T},$$

whence  $p_1^{1-\frac{1}{k}} = p_0^{-\frac{1}{k}} p_2$ ,  $p_1^{k-1} = p_0^{-1} p_2^k$

or  $(k-1) \log p_1 = k \log p_2 - \log p_0$ .

and  $k = \frac{\log p_1 - \log p_0}{\log p_1 - \log p_2}.$

Since  $p_1 > p_2 > p_0$ , we have  $k > 1$ .

If the pressures differ but little from each other, the differences of their logarithms are approximately proportional to the differences of the pressures themselves, and the formula becomes

$$k = \frac{p_1 - p_0}{p_1 - p_2}.$$

The best determinations of  $k$  by this method were made by Röntgen (*Pogg. Ann.*, cxli., 1870).

He worked with a large globe having a capacity of 70 litres. The pressures were measured by a metallic manometer, viz. a corrugated plate of German silver fixed over an opening in the globe. Any movement of the plate due to variation of pressure in the globe was communicated to a mirror attached to the plate, and the deflection angle of the mirror could be measured by means of a telescope and scale. The scale divisions

being preliminarily calibrated, the pressure readings could be directly converted into millimetres of mercury.

In the course of these experiments various questions presented themselves: Whether the velocity of flow had an influence? Whether the change was actually adiabatic? Whether the formulae for ideal gases could be applied? Even the elastic after-effect of the metallic plate was investigated by Röntgen.

The values of  $k$  obtained by Röntgen from a series of experiments with dry atmospheric air at about  $17^\circ$  are

|        |        |
|--------|--------|
| 1.4068 | 1.4032 |
| 1.4036 | 1.4050 |
| 1.4073 | 1.4051 |
| 1.4047 | 1.4049 |
| 1.4063 | 1.4064 |

with a mean  $k=1.4053$ , of which the third decimal is still accurate, the probable error being 0.00027.

Regnault found for air  $c_p=0.2375$  cal. Thus  $c_v$  can be calculated, and since  $c_p - c_v = R$ , the mechanical equivalent of heat can be determined,  $R$  being calculated in energy units

from  $R = \frac{p_0 v_0}{T}$ , where  $p_0$ ,  $v_0$  and  $T$  are introduced through the

specific weight of air at  $0^\circ$  C. and the pressure of 760 mm.; one litre of air weighs then 1.293 gr. If  $p_0$  and  $v_0$  are expressed in c.g.s. units,  $R$  is obtained in ergs. In this manner one finds that 1 gram calorie is equivalent to  $419.10^5$  ergs.

17. Let us now consider the more general case, viz. of a system whose state,  $B$ , is determined, apart from the temperature  $T$ , by any number ( $n$ ) of parameters  $a$ ,  $\beta$ ,  $\gamma$ , etc. The internal energy  $\epsilon$  is a function of all these magnitudes. Thus, the increment of  $\epsilon$  in passing from  $B$  to an indefinitely near state  $B'$ , determined by  $a + da$ ,  $\beta + d\beta$ , . . .,  $T + dT$ , is

$$d\epsilon = \frac{\partial \epsilon}{\partial a} da + \frac{\partial \epsilon}{\partial \beta} d\beta + \dots + \frac{\partial \epsilon}{\partial T} dT. \quad (16)$$

Again, the external work is readily seen to be expressible in the form

$$A da + B d\beta + C d\gamma + \dots + \Theta dT,$$

where  $A$ ,  $B$ ,  $C$ , etc., are functions of the independent variables  $a$ ,  $\beta$ , . . .  $T$ .

Thus, the first law assumes the form

$$dQ = \left( \frac{\partial \epsilon}{\partial \alpha} + A \right) d\alpha + \left( \frac{\partial \epsilon}{\partial \beta} + B \right) d\beta + \dots + \left( \frac{\partial \epsilon}{\partial T} + \Theta \right) dT. \quad (17)$$

Now, the parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc., can be so chosen that the term  $\Theta dT$  does not occur in the expression for the work. In fact, it is always possible to introduce such parameters that, so long as they remain constant, no matter how the temperature varies, no external work is done. If the dynamical reactions between the system and its surroundings are all of the common, mechanical kind, it is enough to take for  $\alpha$ ,  $\beta$ , etc., the geometrical magnitudes which determine the size and the shape of the system including the relative positions of its parts and thus also the position of the points of application of forces. When these magnitudes, which may be called generalised co-ordinates, are kept constant, no external work is being done. As examples of such co-ordinates may be taken, the volume of a body, the length of a rod, its angle of torsion, etc. The coefficients  $A$ ,  $B$ ,  $C$ , etc., may be called generalised force components. Their significance depends upon that of  $\alpha$ ,  $\beta$ , etc. Thus, *e.g.*, if  $\alpha$  be the volume of a gas, the work is  $p d\alpha$ , so that  $A = p$ . Similarly, the force component corresponding to the length of a rod is the force with which the rod tends to expand, and that corresponding to its torsion angle, the moment of rotation exerted by the rod at one of its extremities. Now, we have

$$\frac{dQ}{T} = \frac{1}{T} \left( \frac{\partial \epsilon}{\partial \alpha} + A \right) d\alpha + \frac{1}{T} \left( \frac{\partial \epsilon}{\partial \beta} + B \right) d\beta + \dots + \frac{1}{T} \frac{\partial \epsilon}{\partial T} dT, \quad (18)$$

and this must be, by the second law, a total differential ( $d\eta$ ). Whence follows a number of conditions equal to the number of combinations, two by two, of the independent variables. These conditions split into two groups. One of these consists of relations such as

$$\frac{\partial}{\partial \beta} \left\{ \frac{1}{T} \left( \frac{\partial \epsilon}{\partial \alpha} + A \right) \right\} = \frac{\partial}{\partial \alpha} \left\{ \frac{1}{T} \left( \frac{\partial \epsilon}{\partial \beta} + B \right) \right\},$$

or, since  $T$  is independent of  $\alpha$ ,  $\beta$ ,

$$\frac{\partial A}{\partial \beta} = \frac{\partial B}{\partial \alpha}. \quad \dots \quad (19)$$

Such conditions exist only when there is more than one parameter of the kind of  $\alpha, \beta$ , etc. They express that the force components are the derivatives with respect to  $\alpha, \beta, \gamma$ , etc., of one and the same function,

$$A = \frac{\partial W}{\partial \alpha}, B = \frac{\partial W}{\partial \beta}, \text{ etc.},$$

so that  $A d\alpha + B d\beta + \text{etc.}$  is the total differential of  $W$ , if  $T$  be kept constant. In other words, the work of external forces at constant temperature is a total differential. This could also be deduced more simply. In fact, since for a cycle  $\int \frac{dQ}{T}$  is nil,  $dQ/T$  is a total differential. If, therefore,  $T$  is constant,  $\int dQ = 0$ , so that  $dQ$  and thus also the work are total differentials.

A condition of the second group arises if the last term of (18) is combined with any of the remaining ones. We then have equations of the form

$$\frac{\partial}{\partial \alpha} \left\{ \frac{1}{T} \frac{\partial \epsilon}{\partial T} \right\} = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left( \frac{\partial \epsilon}{\partial \alpha} + A \right) \right\}$$

or, developed,

$$\left( \frac{\partial \epsilon}{\partial \alpha} \right)_{T, \beta \dots} = -A + T \left( \frac{\partial A}{\partial T} \right)_{\alpha, \beta \dots}, \quad . \quad . \quad (20)$$

and similarly,

$$\left( \frac{\partial \epsilon}{\partial \beta} \right)_{T, \alpha \dots} = -B + T \left( \frac{\partial B}{\partial T} \right)_{\alpha, \beta \dots}, \text{ etc.}$$

18. In order to see the meaning of these formulæ let us recall that two kinds of measurements can be made on a body. In the first of these, the calorimetric ones, a quantity of heat is measured, while in the second we are concerned only with the temperature  $T$ , the co-ordinates  $\alpha, \beta$ , etc., and the forces  $A, B$ , etc. The latter kind may be called investigations on elasticity in the broadest sense of the word. Such, for instance, is in the case of a gas the determination of pressure as a function of temperature and volume, and for a stretched body the investigation of the tension as dependent on the dimensions and temperature. Let us now suppose that the elastic investigations have been carried out as completely as possible, so that the force components  $A, B$ , etc., are known as functions of  $\alpha, \beta, \dots, T$ , and let us ask how many calorimetric measurements are necessary in order to find the remaining magnitudes appearing in the

equation, *i.e.* the values of  $\partial\epsilon/\partial a$ ,  $\partial\epsilon/\partial\beta$ ,  $\dots \partial\epsilon/\partial T$ . If these  $n+1$  magnitudes are known for all possible values of  $a$ ,  $\beta$ ,  $\dots T$ , we know also the energy as function of these magnitudes in which, as could be expected, an additive constant remains free.

Let us first see what calorimetric measurements are necessary if no use is made of the second law. Clearly,  $n+1$  calorimetric measurements are required in order to determine by means of equation (17), in which, however,  $\Theta$  no longer occurs, the values of  $\partial\epsilon/\partial a$ ,  $\partial\epsilon/\partial\beta$ ,  $\dots \partial\epsilon/\partial T$  for given values of  $a$ ,  $\beta$ ,  $\dots T$ . The corresponding experiments would consist in starting always from the same initial state, taking  $n+1$  mutually independent combinations of changes  $da$ ,  $d\beta$ ,  $\dots dT$ , and measuring these changes themselves as well as  $dQ$ . By mutually independent combinations are here meant such as yield mutually independent equations between the  $n+1$  derivatives. For this purpose experiments can be used in which always only one of the magnitudes  $a$ ,  $\beta$ ,  $\dots T$  is varied, or also a single experiment at constant  $a$ ,  $\beta$ , combined with  $n$  others in which only  $T$  and  $a$ ,  $T$  and  $\beta$ , and so on, are changed. Some of these experiments could also be arranged adiabatically ( $dQ=0$ ), so that only the changes of  $a$ ,  $\beta$ ,  $\dots T$  would have to be measured.

By repeating these  $n+1$  experiments for all possible initial states, the derivatives of  $\epsilon$  and thus also  $\epsilon$  itself as function of  $a$ ,  $\beta$ ,  $\dots T$  would be found. At the same time one would have the opportunity of testing the law of conservation of energy on the results obtained. Thus, *e.g.*, if both  $\partial\epsilon/\partial a$  and  $\partial\epsilon/\partial\beta$  are known as functions of  $a$ ,  $\beta$ ,  $\dots T$ , the relation

$$\frac{\partial}{\partial\beta}\left(\frac{\partial\epsilon}{\partial a}\right) = \frac{\partial}{\partial a}\left(\frac{\partial\epsilon}{\partial\beta}\right)$$

can be verified.

It goes without saying that if such verifications are not wanted, a smaller number of calorimetric measurements will suffice.

19. The importance of the second law can now be said to consist in enabling us to reduce this number of calorimetric measurements still more. In fact, with the aid of the equations (20) the values of  $\partial\epsilon/\partial a$ ,  $\partial\epsilon/\partial\beta$ , etc., can be determined.

In this manner an expression for  $\epsilon$  of the form

$$\epsilon = F(a, \beta, \dots T) + \phi(T) \quad . \quad . \quad . \quad (21)$$



will be obtained, where only  $\phi(T)$  remains unknown. To solve the problem it is then enough to make at each temperature a single calorimetric measurement in which the initial values of  $\alpha$ ,  $\beta$ , etc., as well as the manner of changing them together with the temperature may be chosen arbitrarily. In fact, one such measurement gives us  $\partial\epsilon/\partial T$  and thus also, by (21), the value of  $d\phi/dT$ .

From these considerations it follows, for instance, that, theoretically, the internal energy and the specific heats of carbon dioxide would be known for all its states, provided the isothermals are completely determined and the specific heat of gaseous carbon dioxide at constant pressure is measured as function of temperature at an arbitrarily chosen pressure.

Needless to say, if more measurements are made than are necessary, the opportunity is afforded for testing the second law in a variety of ways.

Let us now deduce some consequences from the relation

$$\left(\frac{\partial\epsilon}{\partial\alpha}\right)_T + A = T\left(\frac{\partial A}{\partial T}\right)_\alpha$$

found above. By (17),  $\left\{\left(\frac{\partial\epsilon}{\partial\alpha}\right)_T + A\right\}d\alpha$  represents the quantity of heat,  $dQ_\alpha$ , which must be supplied in order to increase  $\alpha$  by  $d\alpha$ . Thus,

$$\frac{dQ_\alpha}{d\alpha} = T\left(\frac{\partial A}{\partial T}\right)_\alpha.$$

The right-hand member indicates how a force varies with temperature, while the left-hand member gives the heat which must be supplied in an isothermal change.

## 20. Application to adiabatic changes.

We may now consider different kinds of adiabatic changes, such as the sudden stretching of a twisted bar, or the sudden twisting of a stretched bar. Each of these adiabatic changes is accompanied by a change of temperature. Let us assume that  $\beta$ ,  $\gamma$ , etc., are constant and that  $\alpha$  and  $T$  only are variable. Then

$$\left\{\left(\frac{\partial\epsilon}{\partial\alpha}\right)_T + A\right\}d\alpha + \left(\frac{\partial\epsilon}{\partial T}\right)_\alpha dT = 0,$$

whence

$$dT = - \frac{\left(\frac{\partial \epsilon}{\partial \alpha}\right)_T + A}{\left(\frac{\partial \epsilon}{\partial T}\right)_\alpha} d\alpha.$$

This formula gives the change of temperature associated with the adiabatic change of one of the co-ordinates. The coefficient  $\left(\frac{\partial \epsilon}{\partial T}\right)_\alpha$  is the specific heat for constant parameters; we may assume that this is measurable, while  $\left(\frac{\partial \epsilon}{\partial \alpha}\right)_T + A$  cannot be measured directly. By (20), however, we can write

$$dT = - \frac{T \left(\frac{\partial A}{\partial T}\right)_\alpha}{\left(\frac{\partial \epsilon}{\partial T}\right)_\alpha} d\alpha, \quad (22)$$

where all the magnitudes can be measured.

Let us apply this formula to water. If  $\alpha$  stands for the volume and  $A$  for the pressure, then

$$dT = - T \left(\frac{\partial p}{\partial T}\right)_v \frac{dv}{c_v}.$$

This formula, however, is not very convenient for applications, since  $dv$  is difficult to measure. We will transform it, therefore, but we prefer to return for this purpose to the more general case.

Let, then,  $\beta, \gamma$ , etc., be again constant, and let  $\alpha$  vary. This will give rise to a change of  $T$  which will be accompanied by a change of the force  $A$ . Since the force  $A$  is a function of  $\alpha, \beta, \dots T$ , we have

$$dA = \left(\frac{\partial A}{\partial \alpha}\right)_T d\alpha + \left(\frac{\partial A}{\partial T}\right)_\alpha dT,$$

and substituting here the value of  $d\alpha$  from formula (22),

$$dA = \left\{ - \frac{1}{T} \left(\frac{\partial A}{\partial \alpha}\right)_T \frac{\left(\frac{\partial \epsilon}{\partial T}\right)_\alpha}{\left(\frac{\partial \epsilon}{\partial T}\right)_\alpha} + \left(\frac{\partial A}{\partial T}\right)_\alpha \right\} dT, \quad (23)$$

which gives the change of temperature due to a sudden change of the force  $A$ .

In order to see the meaning of (23) we will determine the specific heat at constant  $\beta$ ,  $\gamma$ , . . . and  $A$ . Now,

$$dQ = \left\{ \left( \frac{\partial \epsilon}{\partial a} \right)_T + A \right\} da + \left( \frac{\partial \epsilon}{\partial T} \right)_a dT.$$

Again, for constant  $A$ ,

$$dA = \left( \frac{\partial A}{\partial a} \right)_T da + \left( \frac{\partial A}{\partial T} \right)_a dT = 0,$$

so that

$$da = - \frac{\left( \frac{\partial A}{\partial T} \right)_a}{\left( \frac{\partial A}{\partial a} \right)_T} dT. \quad (24)$$

Substituting this value of  $da$  and that found before for  $\left( \frac{\partial \epsilon}{\partial a} \right)_T + A$  into the expression for  $dQ$ , we have

$$dQ = \left\{ -T \frac{\left( \frac{\partial A}{\partial T} \right)_a^2}{\left( \frac{\partial A}{\partial a} \right)_T} + \left( \frac{\partial \epsilon}{\partial T} \right)_a \right\} dT.$$

The bracketed expression is the specific heat at constant  $A$  and may be denoted by  $c_A$ . Thus, combining this result with (23),

$$dA = - \frac{1}{T} \frac{\left( \frac{\partial A}{\partial a} \right)_T}{\left( \frac{\partial A}{\partial T} \right)_a} c_A dT$$

or, by (24),

$$dT = -T \frac{\left( \frac{\partial A}{\partial T} \right)_a}{\left( \frac{\partial A}{\partial a} \right)_T c_A} dA = \frac{T}{c_A} \left( \frac{\partial a}{\partial T} \right)_A dA. \quad (25)$$

This is the classical formula for the change of temperature in an adiabatic process.

21. We will now give some applications of formula (25). In the first place let us consider the adiabatic compression of liquids on which many experiments were made by Joule. In this case the formula becomes

$$dT = \frac{1}{c_p} T \left( \frac{\partial v}{\partial T} \right)_p dp = \frac{\alpha v T}{c_p} dp, \quad (26)$$

where  $\alpha$  is the dilatation coefficient at constant pressure. An increase of pressure is, in general, accompanied by a rise of temperature. An exception is water below  $4^\circ$ ,  $\alpha$  being then negative.

Many experiments of this kind were made by Joule. He increased the pressure suddenly by placing weights upon a piston and measured the corresponding change of temperature by means of a thermopile. Rigorously, for a non-infinitesimal increase of pressure formula (26) would have to be integrated. Since, however, the volume of a liquid is but very slightly reduced by an increase of pressure and since also the accompanying change of temperature is very small, we may safely write for a finite pressure variation

$$\Delta T = \frac{\alpha v T}{c_p} \Delta p.$$

Joule worked with fish-oil. Some of his results are given below.

| $\Delta p$ in kg. per cm. <sup>2</sup> | Initial temp.<br>in degr. C. | $\Delta T$ obs. | $\Delta T$ calc. |
|----------------------------------------|------------------------------|-----------------|------------------|
| 8.19                                   | 16.00                        | 0.0792          | 0.0886           |
| 16.17                                  | 17.27                        | 0.1686          | 0.1758           |
| 29.17                                  | 16.27                        | 0.2663          | 0.2837           |

$$c_p = 0.5223 \text{ calory,}$$

$$\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = 0.0007582.$$

Still more interesting are Joule's experiments with water, which yielded the following results :

| $\Delta p$ in kg. per cm. <sup>2</sup> | Initial temp.<br>in degr. C. | $\Delta T$ obs. | $\Delta T$ calc. |
|----------------------------------------|------------------------------|-----------------|------------------|
| 26.19                                  | 1.20                         | -0.0083         | -0.0071          |
| 26.19                                  | 5.00                         | 0.0044          | 0.0027           |
| 26.19                                  | 11.69                        | 0.0205          | 0.0197           |
| 26.19                                  | 18.38                        | 0.0314          | 0.0340           |
| 26.19                                  | 30.00                        | 0.0544          | 0.0563           |
| 26.17                                  | 31.17                        | 0.0394          | 0.0353           |
| 26.17                                  | 40.40                        | 0.0450          | 0.0476           |

These results formed one of the first experimental verifications of the second law. Without the aid of this law the outcome of the experiments could not be foreseen. One could then say

only that due to the work done upon the liquid in an adiabatic compression the internal energy which depends on volume and temperature will increase, but not how this will affect the temperature. The remarkable thing is that through an adiabatic compression of water below  $4^{\circ}$  C. the temperature falls in spite of the increase of the internal energy.

22. Another series of experiments concerns the adiabatic stretching of wires. The co-ordinate  $a$  is in this case the length  $l$ , and the force  $A$  is  $-P$ , the negative tension, since in a dilatation  $dl$  the work done by the wire is  $-Pdl$ . Thus,

$$dT = -\frac{T}{c_p} \left( \frac{\partial l}{\partial T} \right)_p dP.$$

Here  $c_p$  is the heat required for raising the temperature of the whole wire by  $1^{\circ}$ . If the tension is gradually increased from  $P_0$  to  $P$ , then

$$T - T_0 = - \int_{P_0}^P \frac{T}{c_p} \left( \frac{\partial l}{\partial T} \right)_p dP,$$

which may be written

$$T - T_0 = -\frac{T}{c_p} \left( \frac{\partial l}{\partial T} \right)_p (P - P_0). \quad . \quad . \quad . \quad (27)$$

Experiments of this kind were made by Joule. His results, however, were not quite good. The best results gave Haga's experiments (*Wied. Ann.*, xv., 1882).

In these experiments the change of temperature of the stretched wire was measured by means of a thermopile formed by the wire itself and another thin wire wound around it. The results were compared with the formula

$$\Delta T = -\frac{Ta}{Awc_p} \Delta P,$$

where  $A$  is the mechanical equivalent of heat and  $w$  the mass of a unit length of the wire. This agrees with (27). For, since  $c_p$  in (27) is the heat capacity of the whole wire expressed in mechanical units, we had to replace it by  $Alwc_p$ , if  $c_p$  is to be taken per unit mass and to be expressed in calories. Further,

$$\left( \frac{\partial l}{\partial T} \right)_p = al.$$

For the drop of temperature of a steel wire of 1.6 mm. in



diameter, stretched by a weight of 21.715 kg. at a temperature of  $17.1^{\circ}\text{C}$ ., Haga found the values

0.1042, 0.1050, 0.1046, 0.1051, 0.1018, 0.1043, 0.1026, 0.1030, with a mean of  $\Delta T = -0.1038$ .

Another set of experiments with the same tension and at  $t = 17^{\circ}\text{C}$ . gave him the mean value  $\Delta T = -0.1049$ , and yet another, at  $t = 16.70^{\circ}\text{C}$ .,  $\Delta T = -0.1054$ .

For a German-silver wire of 0.105 mm. in diameter and a tension of 13.05 kg. Haga found the mean value  $\Delta T = -0.1063$ , and for the tension of 21.30 kg.,  $\Delta T = -0.1725$ . These results confirm the proportionality of the change of temperature and the tension. In fact, they give for the decrease of temperature per kg. the values 0.00814 and 0.00812 respectively. Finally, the values of  $c_p$  and  $w$  as well as the expansion coefficients of the steel and the German-silver wire being accurately determined, the formula was used for calculating  $A$ .

From the experiments with the steel wire Haga found for  $A$  the value 437.8, and from those with the German-silver wire, 428.1, with the kilogram meter as unit of work. To replace this by the erg as unit, the figures have to be multiplied by  $981 \cdot 10^{12}$ . Thus the results become  $429 \cdot 10^5$  and  $420 \cdot 10^5$ . Actually the mechanical equivalent of heat is  $419 \cdot 10^5$ .

India-rubber, when moderately stretched, has a negative expansion coefficient. It can thus be expected to become warmer through a further adiabatic stretching, which is verified by experiment and can even be felt with the lips.

23. Formula (25) could also be derived directly. If instead of  $\alpha, \beta, \gamma \dots T$  the magnitudes  $A, \beta, \gamma \dots T$  are taken as independent variables, then

$$dQ = \left( \frac{\partial \epsilon}{\partial A} + A \frac{\partial \alpha}{\partial A} \right) dA + \left( \frac{\partial \epsilon}{\partial \beta} + B + A \frac{\partial \alpha}{\partial \beta} \right) d\beta + \dots + \left( \frac{\partial \epsilon}{\partial T} + A \frac{\partial \alpha}{\partial T} \right) dT.$$

Thus, for an adiabatic change in which  $A$  and  $T$  only are varied,

$$dT = - \frac{\left( \frac{\partial \epsilon}{\partial A} \right)_T + A \left( \frac{\partial \alpha}{\partial A} \right)_T}{\left( \frac{\partial \epsilon}{\partial T} \right)_A + A \left( \frac{\partial \alpha}{\partial T} \right)_A} dA.$$

The numerator can be transformed by applying again the second

law, *i.e.* by recalling that  $dQ/T$  is a total differential. This gives the relation

$$\frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[ \left( \frac{\partial \epsilon}{\partial A} \right)_T + A \left( \frac{\partial \alpha}{\partial A} \right)_T \right] \right\} = \frac{\partial}{\partial A} \left\{ \frac{1}{T} \left[ \left( \frac{\partial \epsilon}{\partial T} \right)_A + A \left( \frac{\partial \alpha}{\partial T} \right)_A \right] \right\},$$

$$\begin{aligned} i.e. \quad \frac{1}{T} \left\{ \frac{\partial^2 \epsilon}{\partial T \partial A} + A \frac{\partial^2 \alpha}{\partial T \partial A} \right\} - \frac{1}{T^2} \left\{ \left( \frac{\partial \epsilon}{\partial A} \right)_T + A \left( \frac{\partial \alpha}{\partial A} \right)_T \right\} \\ = \frac{1}{T} \left( \frac{\partial^2 \epsilon}{\partial A \partial T} + A \frac{\partial^2 \alpha}{\partial A \partial T} + \frac{\partial \alpha}{\partial T} \right) \end{aligned}$$

$$\text{or} \quad \left( \frac{\partial \epsilon}{\partial A} \right)_T + A \left( \frac{\partial \alpha}{\partial A} \right)_T = -T \left( \frac{\partial \alpha}{\partial T} \right)_A.$$

Substituting this for the numerator and noticing that the denominator

$$\left( \frac{\partial \epsilon}{\partial T} \right)_A + A \left( \frac{\partial \alpha}{\partial T} \right)_A$$

is the coefficient of  $dT$  in the expression for  $dQ$  and represents therefore the specific heat at constant  $A$ ,  $c_A$ , we find

$$dT = \frac{T}{c_A} \left( \frac{\partial \alpha}{\partial T} \right)_A dA,$$

which is the required formula (25).

For an exercise one may take all the forces for the independent variables. In the most general way any magnitudes whatever, but in sufficient number, could be chosen as variables without specifying whether they are forces or parameters.

#### 24. Application to a liquid film.

Let us consider a plane liquid film. Its state will be completely determined by its area  $\sigma$  and temperature  $T$ . If  $2H$  be the tension of the film per unit length, the work done by the system is  $-2Hd\sigma$ , so that in formula (20)  $A$  is to be replaced by  $-2H$  and  $\alpha$  by  $\sigma$ . This gives

$$\left( \frac{\partial \epsilon}{\partial \sigma} \right)_T = 2H - 2T \frac{\partial H}{\partial T}. \quad (28)$$

If it were a problem in statics, one would simply have

$$2H = \left( \frac{\partial \epsilon}{\partial \sigma} \right)_T.$$

Let us apply to this case equation (17). Putting  $dT=0$  and making use of (28), we find

$$dQ = -2T \frac{\partial H}{\partial T} d\sigma.$$



so that, if  $S$  be the area of either plate, the energy of the condenser amounts to

$$\frac{1}{2} \frac{E^2 S}{d}.$$

If now  $d$  is changed by  $\delta d$ , the change of the energy is

$$-\frac{1}{2} \frac{E^2 S}{d^2} \delta d, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and this must be equal to the sum of the work done by the element and the external work done in displacing the plates relatively to each other. The latter work is

$$\frac{1}{2} \frac{E^2 S}{d^2} \delta d : \quad . \quad . \quad . \quad . \quad . \quad (31)$$

for the tension along the lines of force is given by (29), so that the attraction between the plates is  $\frac{1}{2} \frac{E^2 S}{d^2}$ .

To find the work done by the element we have to subtract (31) from (30), and since the charge of the plate  $P$  is  $ES/d$ , and therefore,  $de = -\frac{ES}{d^2} \delta d$ , the result is

$$Ede.$$

This holds good for any choice of the units, provided the unit of electric charge and that of potential difference or electromotive force correspond to each other.

We now have

$$dQ = \frac{\partial \epsilon}{\partial e} de + \frac{\partial \epsilon}{\partial T} dT + Ede,$$

whence we can deduce some further relations by either using the property of  $dQ/T$  as a total differential or by applying the relation (20) found before.

Thus we find

$$\frac{\partial \epsilon}{\partial e} = -E + T \frac{dE}{dT}, \quad . \quad . \quad . \quad . \quad (32)$$

where  $\frac{dE}{dT}$  has been written for  $\left(\frac{\partial E}{\partial T}\right)_e$ , the electromotive force being assumed not to be altered by the passage of electricity.

The last result differs from that of the older theory which gave the relation

$$\frac{\partial \epsilon}{\partial e} = -E. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

This simple rule is derived under the assumption that  $dQ$  and  $dT$  are both zero. If, in spite of this, formula (33) stands the test of some experiments, it is only because in these  $dE/dT$  is very small.

Using equation (32) we can now write

$$dQ = T \frac{dE}{dT} de + \left( \frac{\partial \epsilon}{\partial T} \right)_e dT.$$

Whence we see that in order to keep the temperature constant while electricity is being transferred, heat must be supplied to or taken from the element. The heat to be supplied per unit of transferred electricity is  $T \frac{dE}{dT}$ . If, therefore,  $dE/dT$  is positive, the temperature would fall if during the passage of electricity towards the positive pole no heat were supplied. In this case then the element absorbs heat. If the element is traversed by a constant current  $i$ , the absorption per unit time is  $T \frac{dE}{dT} i$ .

Exactly because the possibility of such a heat effect, proportional to the first power of the intensity of the current, was overlooked, the older theory, starting from the energy law, gave the equation (33).

26. Returning once more to formula (20),

$$\left( \frac{\partial \epsilon}{\partial a} \right)_T + A = T \left( \frac{\partial A}{\partial T} \right)_a,$$

let us apply it to the case of a substance forming two phases which are in equilibrium. The parameter  $a$  can now be replaced by the volume  $v$ , and  $A$  by the pressure  $p$ . The pressure will in this case depend on the temperature alone and not on the volume.

Thus we can write

$$\left( \frac{\partial \epsilon}{\partial v} \right)_T + p = T \frac{dp}{dT}. \quad . \quad . \quad . \quad . \quad (34)$$



The first law gives in this case

$$dQ = \left( \frac{\partial \epsilon}{\partial T} \right)_v dT + \left\{ \left( \frac{\partial \epsilon}{\partial v} \right)_T + p \right\} dv,$$

so that  $\left( \frac{\partial \epsilon}{\partial v} \right)_T + p$  is the heat to be supplied when at constant temperature the volume increases, reckoned per unit of volume increment. Let  $v_1$  be the specific volume (*i.e.* the volume of a mass unit) of the first phase and  $v_2$  that of the second phase, and let  $v_1 > v_2$ . When the volume increases, a certain quantity of the substance will pass from the second into the first phase, and to find the quantity expressed in mass units, the volume increment has to be divided by  $v_1 - v_2$ . Thus, if  $r$  be the heat required for this change, per unit mass, formula (34) will give

$$T \frac{dp}{dT} = \frac{r}{v_1 - v_2}. \quad . \quad . \quad . \quad . \quad (35)$$

This is Clapeyron's equation, one of the most remarkable formulæ of thermodynamics. It was first applied to the case of a liquid and its vapour,  $r$  being then the latent heat of evaporation expressed in ergs.

Which of the two phases is called the first, does not matter. For  $r$  changes its sign together with  $v_1 - v_2$ .

27. Clausius has applied this formula in order, *e.g.*, to calculate  $v_1$  for steam from the pressure at different temperatures determined by Regnault and from the latent heat of evaporation, the volume  $v_2$  being known accurately enough. He compared the values of the specific volume of steam thus found with those determined experimentally by Fairbairn and Tate. As will be seen from the following figures, the agreement is satisfactory.

| Temp. in degrees C. | Vol. of 1 gram in cm. <sup>3</sup> |             |
|---------------------|------------------------------------|-------------|
|                     | Observed.                          | Calculated. |
| 58.2                | 8275                               | 8230        |
| 77.18               | 3723                               | 3740        |
| 86.83               | 2623                               | 2600        |
| 117.16              | 943                                | 947         |
| 124.16              | 759                                | 769         |
| 131.77              | 606                                | 619         |
| 139.21              | 497                                | 505         |
| 144.74              | 450                                | 437         |

The computation of the latent heat of evaporation for water at  $100^\circ$  may be left to the reader. From Regnault's experiments one finds that in the neighbourhood of this temperature  $\frac{dp}{dT} = 27.2$  (mm. mercury). Further,  $v_1 = 1658 \text{ cm.}^3$ , and we can put  $v_2 = 1 \text{ cm.}^3$ , which in relation to  $v_1$  is accurate enough. A gram calory is equivalent to  $419.10^5$  ergs.

The result will be  $r = 535.8$ , while Regnault's measurements gave  $r = 537$ .

Let us now consider the case of a solid and a liquid phase in equilibrium. Call the liquid phase the first; then  $r$  will be the latent heat of melting and will be positive. If melting is accompanied by an increase of volume, then, by (35), the melting temperature (freezing point) will rise with increased pressure. In the case of ice and some other substances melting is accompanied by contraction, so that by increasing the pressure the melting point is lowered.

This was tested experimentally by Kelvin. Some of his results for water are :

| Increase of pressure. | Depression of freezing point in $^\circ \text{C.}$ |             |
|-----------------------|----------------------------------------------------|-------------|
|                       | Observed.                                          | Calculated. |
| 8.1 alm.              | 0.0580                                             | 0.0607      |
| 16.8                  | 0.1289                                             | 0.1260      |

Kelvin himself considered this good agreement between theory and experiment as due partly to chance, since his experiments were not very accurate.

28. Among the most beautiful experiments of this kind are those with acetic acid made by de Visser and described in his dissertation entitled *Experiments with the Manokryometer* (1891). The melting point of acetic acid is  $16.5^\circ$ . The experiments can therefore be made at room temperature, so that the exchange of heat with the surroundings will be small.

The apparatus used by de Visser and called by him manokryometer consisted of a glass reservoir containing the acid and connected with a closed air manometer; the contact between the acetic acid and air was prevented by mercury. The experiments were made at temperatures at which the acetic acid was always partly solid and partly liquid. When through an increase of temperature part of the solid acid is melted, an

increase of pressure is produced as a consequence of the accompanying increase of volume, so that at the higher temperature a new equilibrium of solid and liquid is established.

The ratio  $r/(v_1 - v_2)$  was measured by means of an acetic-acid calorimeter arranged very much like Bunsen's ice calorimeter. Moreover,  $r$  and  $v_1 - v_2$  were also separately determined.

As a result of his experiments de Visser finds for the rise of the melting point, corresponding to an increase of pressure by 1 atmosphere,  $0.02432^\circ \text{C.}$ , while formula (35) with the observed value of  $r, (v_1 - v_2)$  gives  $0.02421^\circ \text{C.}$  The difference between theory and experiment is thus very small.

29. *Regelation of ice.*—Everybody knows the experiment with a copper wire slung over a block of ice. When the joined ends of the wire are weighted, the wire sinks through the ice and the ice freezes over it again. The elementary explanation of this experiment is known. A more accurate treatment discloses the following details :

The sinking wire is always surrounded by a thin layer of water. Suppose the part of the wire within the ice to be horizontal and lay a plane perpendicular to it. Let  $A$  be the lowest,  $B$  the highest point of the circular section of the wire, and  $P$  any point on the circumference determined by the central angle  $\phi$  corresponding to the arc  $AP$ . The pressure in the water layer decreases gradually from  $A$  to  $B$ , proportionally to  $\cos \phi$ . Since water and ice are throughout in contact with each other, the temperature is everywhere equal to the melting point corresponding to the pressure at the given place. The temperature, therefore, increases from  $A$  to  $B$ , again proportionally to  $\cos \phi$ . Under these circumstances there will be heat conduction from  $B$  to  $A$  by three different ways: across the metal, along a roundabout way through the ice, and through the water layer. If the first of these preponderates, we can find from the conductivity of the metal how much heat per second is taken from above and how much arrives below, and thence also the quantities of ice melted below and formed above. These quantities will be equal to each other.

The thickness of the water layer will adjust itself so that the amount of water produced on the lower side of the wire by melting will just be able to stream away under the action of the prevailing pressure difference. This, then, will depend on

the coefficient of viscosity of water. The calculation here indicated was carried out by Ornstein. Corresponding experiments were made by Meerburg.

30. *Boltzmann's law*.—Let us apply formula (12) or (20) to the case of *radiation*. We imagine a perfectly black body  $M$  contained in an evacuated enclosure with perfectly reflecting inner walls. The enclosure is traversed in all directions by rays, it is filled with “black body radiation”. We suppose that, while the state remains otherwise unaltered, heat can be supplied, and that the enclosure can expand. We may assume that the radiation is throughout the same, at least if the wave-lengths are small compared with the dimensions of the enclosure. The aether will contain a certain amount of energy which, per unit volume, will be denoted by  $U$ .

There is a certain analogy between radiation and a gas. The energy of both depends on temperature, and both exert a pressure.

According to the electromagnetic theory of light the pressure of radiation is  $\frac{1}{3}U$ .

Let the enclosure be allowed to expand adiabatically, so that its temperature will fall. If this change is followed by an isothermal expansion, then by an adiabatic compression and finally by an isothermal compression bringing everything back to the original state, the system will have completed a Carnot cycle, and formula (12) will again be applicable.

In the isothermal expansion  $v$  increases by  $dv$ , say, while  $U$  and  $p$  remain unaltered. The energy increases by  $Udv$ , so that

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = U.$$

Equation (12) becomes, therefore,

$$U = T \frac{dp}{dT} - p = \frac{1}{3} T \frac{dU}{dT} - \frac{1}{3} U$$

$$\text{or} \quad T \frac{dU}{dT} = 4U,$$

$$\text{whence} \quad U = CT^4.$$

Thus, the energy of the black body radiation per unit volume is proportional to the fourth power of the absolute temperature, a law already deduced by Stefan from experiments before it was proved theoretically by Boltzmann.

The results in the preceding cases were all obtained by means of formula (20), which in its turn was derived from the property that  $\int \frac{dQ}{T}$  vanishes for a cycle of reversible changes. We might also have obtained these results by considering in each case a Carnot cycle and applying the equation  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$  with  $T_1$  and  $T_2$  differing very little from each other.

31. Let us now pass to those forms of the second law in which the concept of entropy and the associated concepts of free energy and thermodynamical potential play a relevant part.

It was proved before that for a cycle of reversible changes  $\int \frac{dQ}{T} = 0$ . Whence it followed (p. 22) that, if there are two reversible paths leading from  $A$  to  $B$ , the value of  $\int \frac{dQ}{T}$  must be the same for both. If the states of a given system are referred to a normal state  $A$ , then  $\int_A^B \frac{dQ}{T} = \eta$  is the *entropy* in a state  $B$ , the integral being extended over a reversible path from  $A$  to  $B$ .

To take an example, let us determine the entropy for a mass unit of a perfect gas. In this case  $\left(\frac{\partial \epsilon}{\partial v}\right)_T = 0$ , and therefore (cf. p. 7),

$$dQ = c_v dT + p dv.$$

Eliminating  $p$  by the Boyle-Gay Lussac law  $p v = R T$ , we have

$$dQ = c_v dT + \frac{R T}{v} dv$$

$$\text{and} \quad \eta = \int \frac{dQ}{T} = \int \frac{c_v dT}{T} + \int \frac{R dv}{v} = c_v \log \frac{T}{T_0} + R \log \frac{v}{v_0}, \quad (36)$$

where  $v_0$  and  $T_0$  denote the volume and the temperature in the normal state.

We have here assumed that  $c_v$  is independent of volume, which is correct. For since  $\epsilon$  does not depend on the volume, the same is true of  $\partial \epsilon / \partial T$ .

Let us now consider the change of entropy in some simple cases.



If the temperature is constant,  $\eta = R \log \frac{v}{v_0}$ . The entropy of the gas increases then with increasing volume.

If heat is directly supplied to a body, then  $\frac{dQ}{T} = \frac{cdT}{T}$ , and the change of entropy is thus readily determined.

The entropy of a body is, in general, determined only by its pressure, volume, temperature, etc., while the position and the motion of the body as a whole do not matter.

32. We will now prove the following theorem :

The entropy of an isolated system of bodies cannot diminish ; it can only remain constant or increase.

If the system consists of several bodies, this proposition holds good for the total entropy of all these bodies. The entropy of a system of two bodies is the sum of their entropies.

As an example may be taken two bodies of which one gives up heat to the other by conduction. Let  $T_1$  and  $T_2$  be their temperatures, and let  $T_1 > T_2$ . If by conduction or radiation a quantity of heat  $dQ$  passes from the first to the second body, the entropy of the former diminishes by  $dQ/T_1$  and that of the latter increases by  $dQ/T_2$ , so that the total entropy increases by  $\frac{dQ}{T_2} - \frac{dQ}{T_1}$ , which is positive.

To come to the general proof let us remember (p. 21) that for any cycle  $\int \frac{dQ}{T} \leq 0$ , and that, therefore, for a reversible cycle the only possibility left was  $\int \frac{dQ}{T} = 0$ . For a non-reversible cycle, however,  $\int \frac{dQ}{T} < 0$ .

Let now an arbitrary system pass in one way or another from a state  $A$  to a state  $B$ , the temperature at any given instant being assumed to be the same throughout the system. If the system is then brought back from the state  $B$  to the state  $A$  *along a reversible path*, we shall have a complete cycle to which the general theorem just quoted can be applied. Notice that the passage from  $A$  to  $B$  is to be considered as a *real* change about which we wish to learn something, while the passage from  $B$  to  $A$  is merely *fictitious*. The latter being reversible,

the value of the integral  $\int_A^B \frac{dQ}{T}$  taken along it is  $\eta_A - \eta_B$ , so that we have for the whole cycle

$$\int_A^B \frac{dQ}{T} + \eta_A - \eta_B \leq 0,$$

and therefore, for the passage from  $A$  to  $B$ ,

$$\int_A^B \frac{dQ}{T} \leq \eta_B - \eta_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

(while the fictitious passage from  $B$  to  $A$  can henceforth be disregarded). For an *adiabatic* process  $\int_A^B \frac{dQ}{T} = 0$ , and formula (37) becomes

$$\eta_B \geq \eta_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Thus in an *adiabatic* process the entropy cannot diminish. It remains constant if the process is reversible.

We have thus proved that the entropy of an isolated system which, that is, receives no heat from outside, cannot diminish. Thus also the entropy of the universe, which is an isolated system, cannot diminish.

33. If we now consider an *isothermal* change, we can write, by (37),

$$\frac{1}{T} \int_A^B dQ + \eta_A - \eta_B \leq 0$$

or, applying the first law,

$$\epsilon_B - \epsilon_A + W_{AB} + T(\eta_A - \eta_B) \leq 0,$$

where  $W_{AB}$  is the work done by the system.

Thus, putting

$$\epsilon - T\eta = \Psi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

which is the *free energy*, we have

$$\Psi_B - \Psi_A + W_{AB} \leq 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

More especially, if also  $W_{AB} = 0$ , then

$$\Psi_B \leq \Psi_A, \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

that is to say, in an *isothermal* process in which no work is being done the free energy does not increase. It remains constant if the process is reversible. If in particular the only external force is a pressure  $p$ , this result holds good for changes

at constant volume. For then  $W_{AB}=0$ . In the general case considered in Art. 17 the work would be zero if  $\alpha$ ,  $\beta$ , etc., were kept constant.

34. Let us now consider an isothermic change in which not  $\alpha$ ,  $\beta$ , etc., but  $A$ ,  $B$ , etc., remain constant. The work will then be expressed by

$$W_{AB}=A(\alpha_B-\alpha_A)+B(\beta_B-\beta_A)+\dots,$$

and if we put

$$\zeta=\Psi+A\alpha+B\beta+\dots,$$

then, by (40),

$$\zeta_B\leq\zeta_A. \quad (42)$$

The function  $\zeta$  thus defined is called *the thermodynamical potential*. This, then, cannot increase if the temperature and the external forces are kept constant.

In those cases in which the work can be expressed by  $p dv$  the potential becomes

$$\zeta=\Psi+p v=\epsilon-T \eta+p v. \quad (43)$$

By means of this function a variety of questions can be treated. For a homogeneous substance in a state of equilibrium  $\zeta$  has a determined value. If the state of the substance undergoes an infinitesimal change, the corresponding change of  $\zeta$  is, by (43),

$$d \zeta=d \epsilon-T d \eta-\eta d T+p d v+v d p,$$

and since  $d Q=d \epsilon+p d v=T d \eta$ ,

$$d \zeta=-\eta d T+v d p.$$

If  $p$  and  $T$  are taken as independent variables, then,  $d \zeta$  being the total differential of  $\zeta$ ,

$$\left(\frac{\partial \zeta}{\partial T}\right)_p=-\eta \text { and } \left(\frac{\partial \zeta}{\partial p}\right)_T=v. \quad (44)$$

With another choice of independent variables, as e.g.  $v$  and  $T$ , the state of affairs is less simple. We then have

$$d p=\left(\frac{\partial p}{\partial T}\right)_v d T+\left(\frac{\partial p}{\partial v}\right)_T d v,$$

and therefore,

$$d \zeta=\left[-\eta+v\left(\frac{\partial p}{\partial T}\right)_v\right] d T+v\left(\frac{\partial p}{\partial v}\right)_T d v,$$

whence

$$\left(\frac{\partial \zeta}{\partial T}\right)_v=-\eta+v\left(\frac{\partial p}{\partial T}\right)_v,$$

$$\left(\frac{\partial \zeta}{\partial v}\right)_T=v\left(\frac{\partial p}{\partial v}\right)_T.$$

The most convenient independent variables for the free energy are  $v$  and  $T$ . These give the simplest form of the equations. From (39) follows

$$d\Psi = d\epsilon - Td\eta - \eta dT,$$

and since  $Td\eta = d\epsilon + pdv$ ,

$$d\Psi = -pdv - \eta dT,$$

whence 
$$\left(\frac{\partial\Psi}{\partial v}\right)_T = -p, \quad \left(\frac{\partial\Psi}{\partial T}\right)_v = -\eta. \quad . \quad . \quad . \quad (45)$$

The entropy will be best considered as a function of  $\epsilon$  and  $v$ . In fact,

$$d\eta = \frac{d\epsilon}{T} + p\frac{dv}{T},$$

so that 
$$\left(\frac{\partial\eta}{\partial\epsilon}\right)_v = \frac{1}{T}, \quad \left(\frac{\partial\eta}{\partial v}\right)_\epsilon = \frac{p}{T}. \quad . \quad . \quad . \quad (46)$$

If  $\zeta$  were actually given as a function of  $p$  and  $T$ , all other magnitudes could be determined by means of it. In fact,

$$v = \left(\frac{\partial\zeta}{\partial p}\right)_T, \quad \eta = -\left(\frac{\partial\zeta}{\partial T}\right)_p, \quad \epsilon = \zeta - T\left(\frac{\partial\zeta}{\partial T}\right)_p - p\left(\frac{\partial\zeta}{\partial p}\right)_T. \quad . \quad (47)$$

Thus we can say that everything we may want to know about a body can be derived from  $\zeta = f(p, T)$ .

If the body undergoes a change at constant temperature and constant pressure, the quantity of heat to be supplied can be derived from the equation

$$\epsilon = \zeta - T\left(\frac{\partial\zeta}{\partial T}\right)_p - p\left(\frac{\partial\zeta}{\partial p}\right)_T,$$

which, by the first of (47), can be written

$$\epsilon + pv = \zeta - T\left(\frac{\partial\zeta}{\partial T}\right)_p. \quad . \quad . \quad . \quad (48)$$

This can be done, for instance, if a body passes suddenly, at constant  $T$  and  $p$ , from one state of equilibrium  $A$  to another  $B$ .

*Example.*—For the state  $A$  take a vessel with sulphuric acid and water above it, the liquids being separated from each other by a membrane. The state  $B$  will then be attained by removing the membrane, when the liquids will combine. The process is not reversible; both the energy and the entropy are altered.

The quantity of heat to be supplied in this change [which will be negative] is, by the law of conservation of energy,

$$Q = \epsilon_B - \epsilon_A + p(v_B - v_A),$$

instead of which we may write, by (48),

$$Q = \left( \zeta - T \frac{\partial \zeta}{\partial T} \right)_B - \left( \zeta - T \frac{\partial \zeta}{\partial T} \right)_A.$$

This can be evaluated if for both states,  $A$  and  $B$ , the thermodynamical potential  $\zeta$  is given as a function of  $p$  and  $T$ .

35. Let us now determine the free energy for a perfect gas. In this case  $pv = RT$ , where  $R$  depends on the amount of the gas.

By (45),

$$\left( \frac{\partial \Psi}{\partial v} \right)_T = -p = -\frac{RT}{v}.$$

Thus, if  $T$  be constant,

$$\Psi = -RT \log v + C, \quad . \quad . \quad . \quad (49)$$

and if we put  $\Psi = 0$  for  $v = 1$ , the constant  $C$  vanishes, so that

$$\Psi = -RT \log v.$$

Thus the free energy diminishes with increasing volume. Let  $m$  be the mass of the gas, so that a mass unit occupies the volume  $v/m$ . Then the free energy per unit mass will be

$$-RT \log \frac{v}{m},$$

and therefore that of the whole mass

$$\Psi = -mRT \log \frac{v}{m}. \quad . \quad . \quad . \quad (50)$$

We will now verify by means of this formula the fundamental property of the free energy.

Let us imagine a vessel whose volume is divided by a membrane into two parts,  $v_1$  and  $v_2$ , containing  $m_1$  and  $m_2$  mass units of the same gas.

Let us remove the membrane. Then, gravity being disregarded, we shall have a homogeneous mixture of  $m_1 + m_2$  mass units occupying the volume  $v_1 + v_2$ . Thus the increase of the free energy will be, by (50),

$$RT \left\{ m_1 \log \frac{v_1}{m_1} + m_2 \log \frac{v_2}{m_2} - (m_1 + m_2) \log \frac{v_1 + v_2}{m_1 + m_2} \right\}.$$



Let this be denoted by  $RT\Phi$ . Then

$$\frac{\partial \Phi}{\partial v_2} = \frac{m_2}{v_2} - \frac{m_1 + m_2}{v_1 + v_2} = \frac{m_2 v_1 - m_1 v_2}{v_2(v_1 + v_2)},$$

and therefore,

$$\frac{\partial \Phi}{\partial v_2} \begin{cases} > \\ = \\ < \end{cases} 0 \text{ for } v_2 \begin{cases} < \\ = \\ > \end{cases} \frac{m_2}{m_1} v_1,$$

whence we see that  $\Phi$  attains for  $v_2 = \frac{m_2}{m_1} v_1$  a maximum. But

then also  $\Phi = 0$ , so that for all other values the expression  $\Phi$  will be negative. Thus, when the difference in density between the two masses of gas is reduced, the free energy diminishes.

Why it does not change after the removal of the membrane if  $\frac{v_1}{m_1} = \frac{v_2}{m_2}$ , is obvious.

36. Rigorously, if we keep to the given definitions, we can speak neither of entropy, nor of free energy and thermodynamical potential in the case of a system which is not in equilibrium. Thus, for example, if a liquid is in contact with its vapour which has not the pressure required for equilibrium, the system cannot be said to have a determined free energy. This case, however, can readily be transformed into another to which our definitions are applicable. In fact, if a partition is placed between the liquid and the vapour, the whole can be attributed a definite free energy equal to the sum of the values of the free energy for each part taken separately. The same artifice can also be applied to other systems consisting of two or more parts or "phases" having different properties and placed next to each other.

The insertion of such a partition produces, no doubt, disturbances in the boundary layer. These, however, can be neglected, provided the thickness of the boundary layer is small compared with the dimensions of the spaces occupied by the liquid and the vapour, and the above reasoning can be applied.

A non-homogeneous gas could be divided by partitions into cells and each of these could be considered as homogeneous. The free energy of the whole could then be defined as the sum of the free energies of these homogeneous parts. This, however, would not be legitimate if external forces produced variations of

density even in spaces as small as, say,  $10^{-6}$  mm.<sup>3</sup>; for a gas mass of such small dimensions has no longer the properties of an ordinary gas.

37. Here is another important question: In deducing the formulae (38), (41), (42) we have said that if the process is reversible the sign of equality holds. Does this mean that for processes which are decidedly not reversible the equality sign can be cancelled and that the magnitude in question ( $\eta$ ,  $\Psi$  or  $\zeta$ ) will actually change in the sense indicated by the formula?

Experiment seems to answer this question in the affirmative. This can be readily seen in simple cases, such as that of a gas rushing into an empty space or of two bodies at different temperatures brought into contact with each other. Thus, though not without a certain reserve, we may enounce the law: In a non-reversible process the entropy increases if no heat is supplied or taken out, the free energy diminishes if the temperature is kept constant and no work is being done, and the thermodynamical potential decreases if the temperature and the external forces are kept constant.

38. *Isothermal changes*.—Limiting ourselves to isothermal changes we can easily prove that for an isothermal cycle  $\int dQ \geq 0$ , which result could also be deduced from  $\int \frac{dQ}{T} \leq 0$  (Art. 13) by making  $T$  constant.

We submit a system  $M$  to an arbitrary isothermal cycle. We give to the reservoir  $R$  the same temperature as the system is assumed permanently to have. In order to supply or to take out heat, no Carnot cycles are needed (cf. Art. 13); this can be accomplished by direct contact. We can now draw the conclusion that  $\int dQ \geq 0$ . For, if  $\int dQ < 0$ , the system would take up from the reservoir a certain quantity of heat, and since it returns to its original state, this heat would be entirely converted into work, which would clash with Kelvin's principle.

If the process is reversible, the sign  $<$  is obviously ruled out. That is to say, in a reversible isothermal cycle heat is on the whole neither supplied nor taken out, and thus also neither negative nor positive work is done.

It was realised a long time ago that an engine which would continually do work, without being kept up by external agencies, is impossible. This would be *perpetual motion*. We now see

that it is equally impossible to make an arrangement in which everything has always the same temperature and which would produce work on the expense of the energy taken from a heat reservoir of the same temperature. This is usually expressed by saying that *perpetual motion of the second kind* also is impossible.

Starting from the theorem just proved we can now again deduce the concept of free energy. We still assume an isothermal reversible process and a heat reservoir  $R$  which is kept at the constant temperature  $T$  and remains in contact with the system under consideration. Since the work in an isothermal reversible cycle is zero, the work for all possible paths between two given states has the same value. This leads us to the conception that the system has in each state  $A$  the capacity for doing a certain amount of work. A normal state  $N$  being chosen for reference, we will call this work, which can be done by the system in passing from the state  $A$  to the state  $N$  along an isothermal reversible path, the free energy of the system in the state  $A$ . This definition resembles very much that of the internal energy of a body, and one might confound them with each other. But to prevent this it is enough to keep in mind the rôle played by the reservoir  $R$ . In fact, the work done in passing from  $A$  to  $N$  is in general *not* equal to the energy lost by the body, but is due, in part or entirely, to the heat taken from the reservoir.

Let us consider an ideal gas. The difference between the internal and the free energy is then particularly striking. Let the gas be closed off by a piston and surrounded by a heat reservoir. The smaller its volume, the more can the gas expand and do work and the greater, therefore, its free energy. On the other hand, the internal energy depends only on the temperature and not on the volume. In the former case the work done in expansion is due not to the energy of the body but to that of the reservoir.

In the case of the system water-steam the free energy becomes even greater, while the internal energy diminishes, and *vice versa*. In fact, when water is changed into steam, the free energy diminishes because the capacity for doing work decreases, whereas the internal energy is increased by evaporation.

39. In order to compare the values  $\Psi_A$  and  $\Psi_B$  of the free energy in two states of equilibrium  $A$  and  $B$ , we imagine the

system carried, always along a reversible isothermal path, first from  $A$  to  $B$  and then into the normal state. Let  $W_{AB}$  be the work done by the system in passing from  $A$  to  $B$ . Since the work done in passing from  $B$  to the normal state is  $\Psi_B$ , the total work is  $W_{AB} + \Psi_B$ . Thus

$$\Psi_A = W_{AB} + \Psi_B$$

or

$$\Psi_A - \Psi_B = W_{AB},$$

a result already found before.

Of course,  $W_{AB}$  can also be negative, when external work is being done upon the body and the free energy increases by an equal amount.

If the states  $A$  and  $B$  are very near each other, then  $\Psi_A - \Psi_B = -d\Psi$ , and therefore,

$$-d\Psi = A da + B d\beta + \dots,$$

where the right-hand number represents the external work (cf. p. 27).

Consequently,

$$A = -\frac{\partial \Psi}{\partial a}, \quad B = -\frac{\partial \Psi}{\partial \beta}, \text{ etc.}$$

Thus, if  $\Psi$  is known as function of the co-ordinates, the force components can be determined.

Notice once more that the above equations hold good for reversible processes only. For irreversible ones the inequality sign has to be used. The free energy can then diminish even if the body does no work; and if it does some work, the free energy diminishes more than would correspond to this work. Again, if work is done upon the body, its free energy increases by less than would correspond to this work, and may even diminish. If a decrease of free energy associated with producing of an equivalent amount of work is considered as *useful*, we may say that in irreversible processes there is a useless dissipation of free energy.

40. We saw that the force components can be considered as the derivatives with respect to the co-ordinates  $a$  of a function of the co-ordinates and the temperature. This function, taken with the negative sign, is the free energy. Whereof many applications can be made. Suppose, for instance, we wish to set up the equations of equilibrium for an elastic body.

For this purpose we can imagine a rectangular parallelepiped cut out from the body and consider the tensions acting upon its faces and the magnitudes  $a$  determining the deformation, *i.e.* the change of the dimensions and the angles. The free energy which is a function of the co-ordinates  $a$  can, for small deformations, be developed into a series of ascending powers of the  $a$ 's. The tensions will then be found by differentiating this series. Now, it appears from all accurately investigated cases that it is enough to proceed with the series for  $\Psi$  only up to terms of the second order. Again, if as normal state is chosen the undeformed state of the body, the term independent of the co-ordinates vanishes, and there being in the normal state no tensions, also the terms of the first order must vanish, so that we can take for  $\Psi$  a homogeneous quadratic function of the deformations.\*

Let us apply this to a twisted and stretched rod. Let  $\lambda$  be the elongation and  $\omega$  the torsion angle. For a given  $\lambda$  the rod will obviously possess the same internal energy and entropy and therefore also the same free energy, whether it is twisted through a given angle in one or in the opposite sense. Consequently,  $\Psi$  cannot contain odd powers of  $\omega$ . Thus,

$$\begin{aligned}\Psi &= k\lambda^2 + p\lambda^3 + q\omega^2 + \epsilon\lambda\omega^2, \\ \frac{\partial\Psi}{\partial\lambda} &= 2k\lambda + 3p\lambda^2 + \epsilon\omega^2, \quad . \quad . \quad . \quad (51) \\ \frac{\partial\Psi}{\partial\omega} &= 2q\omega + 2\epsilon\lambda\omega.\end{aligned}$$

The physical meaning of  $\partial\Psi/\partial\lambda$  is that of the work which must be done upon the rod in order to produce a unit elongation, and this is the tension  $P$ , while  $\partial\Psi/\partial\omega$  represents the work done by an impressed couple in twisting the rod through an angle 1, and is thus equal to the moment  $\Omega$  of this couple. If  $\lambda$  and  $\omega$  stand for  $\alpha$  and  $\beta$ , then  $A = -P$  and  $B = -\Omega$ .

The remarkable thing is that  $P$  and  $\Omega$  are derived from the same function, *viz.*  $\Psi$ . This is expressed mathematically by  $\frac{\partial P}{\partial\omega} = \frac{\partial\Omega}{\partial\lambda}$ . The force required to produce a certain elongation is thus dependent on the angle of torsion and, *vice versa*, the twisting couple depends on the length of the rod. We can

\* [Yet in what follows terms of the third order are retained.]



conclude also that torsion will produce a shortening of the rod. In fact, if  $P=0$ , when there is no external stretching force, we have, by (51) neglecting the term  $3p\lambda^2$  in presence of  $2k\lambda$ ,  $\lambda = -\frac{\epsilon}{2k}\omega^2$ . It is scarcely necessary to say that the effects here considered are very small.

41. The preceding theorems about entropy, free energy, and the thermodynamical potential enable us to set up the conditions for a state of equilibrium.

Suppose that a body or a system of bodies is kept at constant temperature and that the circumstances are such as to exclude the work of external forces. Thus, *e.g.*, if the external force is a uniform pressure exerted upon the surface, let the volume be kept constant. Internal changes can then still take place and the free energy can diminish. If in this manner a state  $A$  is attained in which the free energy is smaller than in all other states differing infinitesimally from  $A$ , then no further change is possible, since it would be accompanied by an increase of the free energy. The state  $A$  is a *state of equilibrium*. It is characterised by a minimum of the free energy and therefore by the vanishing of the change of the free energy for any infinitesimal change starting from this state. The latter condition is to be understood as in the general theory of the minimum of a function. That is to say, if the change of the state of the system is infinitesimal of the first order, the change of the free energy will be infinitesimal of the second order; the change is zero if second-order magnitudes are rejected.

In the same way the condition of equilibrium can be expressed by means of the thermodynamical potential. In this case the temperature and the pressure  $p$ , if such be the only external force, have to be kept constant. It will then follow from what was said at the beginning of Art. 34, that in a state of equilibrium the thermodynamical potential must be a minimum.

Finally, in the case of entropy we have to imagine that during the changes of the system no heat is supplied or withdrawn. Then (by Art. 32) the entropy cannot diminish. In a state of equilibrium it will be a maximum.

It will be kept in mind that only under the said conditions, which differ in the three cases, does the free energy or the thermodynamical potential become a minimum, and the entropy a



maximum. In the case of free energy we have to assume isothermal changes in which no work is being done, in the case of the thermodynamical potential isothermal changes at constant pressure, and in the case of entropy adiabatic changes.

42. The properties of free energy were derived from formula (40) by equating to zero the term  $W_{AB}$  which represented the external work done by the system. Equally simple results are obtained if it is assumed that during the contemplated process work is being done by external forces having a potential  $\chi$ . Then  $W_{AB} = \chi_A - \chi_B$ , and therefore,  $\Psi_B + \chi_B \leq \Psi_A + \chi_A$ .

In this case, then,  $\Psi$  has simply to be replaced by  $\Psi + \chi$ , and one might be tempted to consider the sum  $\Psi + \chi$  as free energy. To avoid confusion, however, we will not follow this plan but shall continue to understand by free energy the magnitude  $\Psi$  which depends only on the internal state of the system. Whenever necessary, the potential energy  $\chi$  will be added. If the system does besides some work  $W'_{AB}$  (against forces other than those related to  $\chi$ ), then

$$(\Psi_B + \chi_B) - (\Psi_A + \chi_A) + W'_{AB} \leq 0.$$

If  $W'_{AB}$  is nil, there will be equilibrium when  $\Psi + \chi$  attains a minimum.

In what sense entropy and free energy can be attributed to a system which is not in equilibrium, was already explained on p. 51.

43. To illustrate these remarks by an example, let us consider a body consisting of a single substance, gaseous or liquid, which occupies a space of invariable volume and is kept at constant temperature. Let the body be acted upon by external forces, such as gravity, and thus possess a potential energy  $\chi$  per unit mass, which will be a function of the co-ordinates of a volume-element  $dS$ . If  $\Psi$  be the free energy per unit mass and  $\rho$  the density, then the sum of the free and the potential energy will be, for a volume-element,  $\rho(\Psi + \chi)dS$ , and for the whole body,

$$\Phi = \int \rho(\Psi + \chi)dS. \quad . \quad . \quad . \quad . \quad (52)$$

The equilibrium will be attained when  $\Phi$  becomes a minimum. In order, therefore, to determine this state, viz. the space distribution of the substance, we consider an infinitesimal change of that state and write for it

$$\delta\Phi = 0.$$

In a given volume-element  $\chi$  will remain constant but  $\rho$  may undergo a change  $\delta\rho$ , and this will produce a change of  $\Psi$ . In fact,  $\Psi$  depends on the volume  $v$  of the mass unit and thus also on  $\rho$ , since  $v = \frac{1}{\rho}$ . Consequently, since  $T$  is constant,

$$\delta\Psi = \frac{\partial\Psi}{\partial v}\delta v = -\frac{1}{\rho^2}\frac{\partial\Psi}{\partial v}\delta\rho.$$

Thus the condition of equilibrium becomes

$$\delta\Phi = \int[(\Psi + \chi)\delta\rho + \rho\delta\Psi]dS = \int\left[\Psi + \chi - \frac{1}{\rho}\frac{\partial\Psi}{\partial v}\right]\delta\rho dS = 0, \quad (53)$$

and this must hold good for all values of  $\delta\rho$  satisfying the condition

$$\int\delta\rho dS = 0,$$

which expresses the invariability of the whole mass,

$$\int\rho dS = M. \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Consequently, the factor of  $\delta\rho dS$  in the integral (53) must have throughout the space the same value, *i.e.*

$$\Psi + \chi - \frac{1}{\rho}\frac{\partial\Psi}{\partial v} = C. \quad . \quad . \quad . \quad . \quad . \quad (55)$$

It remains only to determine the value of  $C$ . This is indeed possible if the free energy is known as a function of  $\rho$  or of  $v$ . In fact, solving (55) for  $\rho$  ( $\rho$  will depend on the co-ordinates, since these appear in  $\chi$ ) and substituting the value of  $\rho$  in (54), we have an equation for  $C$ , the mass  $M$  being given.

Since  $v = 1/\rho$ , the condition (55) can also be written

$$\Psi - v\frac{\partial\Psi}{\partial v} + \chi = C, \quad . \quad . \quad . \quad . \quad . \quad (55a)$$

$$\text{or, by (45),} \quad \Psi + pv + \chi = C, \quad . \quad . \quad . \quad . \quad . \quad (55b)$$

$$\text{or also,} \quad \zeta + \chi = C. \quad . \quad . \quad . \quad . \quad . \quad (55c)$$

This equation agrees with the known condition for statical equilibrium. To see this, notice that  $\chi$  and  $v$  (or  $\rho$ ) depend on the co-ordinates  $x, y, z$ . Differentiating (55a) with respect to  $x$  and remembering that  $C$  is constant, we have

$$\frac{\partial}{\partial v}\left(\Psi - v\frac{\partial\Psi}{\partial v}\right)\frac{\partial v}{\partial x} + \frac{\partial\chi}{\partial x} = \frac{\partial\chi}{\partial x} - v\frac{\partial^2\Psi}{\partial v^2}\frac{\partial v}{\partial x} = \frac{\partial\chi}{\partial x} - v\frac{\partial}{\partial x}\left(\frac{\partial\Psi}{\partial v}\right) = 0.$$

Thus, multiplying by  $\rho$  and taking account of (45),

$$\frac{\partial p}{\partial x} + \rho \frac{\partial \chi}{\partial x} = 0,$$

and two similar equations with  $y$  and  $z$ .

Now, since  $-\frac{\partial \chi}{\partial x}$ ,  $-\frac{\partial \chi}{\partial y}$ ,  $-\frac{\partial \chi}{\partial z}$  are the components of the

external force per unit mass, these equations express the equilibrium between the forces acting upon a volume-element.

For an ideal gas  $pv$  is constant. Equation (55b) expresses then the simple property that in the state of equilibrium the sum of the free and the potential energy per unit mass has throughout the gas the same value. The potential energy in a column of gas subjected to gravity increases upwards, and this increase is just balanced by the decrease of the free energy due to the diminution of density.

44. We will now treat the problem of the preceding article by means of the entropy law. For simplicity let the volume be again constant; the volume-element may then be taken to be invariable. Let  $\epsilon$  and  $\eta$  be the internal energy and the entropy per unit mass at the place of the element  $dS$ , and let  $\eta$  be considered as a function of  $\epsilon$  and  $v$ . The total entropy is

$$\int \frac{1}{v} \eta dS$$

and the condition of equilibrium will be obtained by equating to zero (with the rejection of second-order magnitudes) the variation of this integral for an infinitesimal change in which no heat is supplied or withdrawn. At the same time two supplementary conditions have to be satisfied, namely, besides (54) also

$$\int \frac{1}{v} (\epsilon + \chi) dS = C.$$

For, since no heat is supplied and no work is being done, the total energy of the system has to be kept constant.

In each volume-element  $v$  and  $\epsilon$  can vary, the latter through the variations of density as well as of temperature.

The required condition thus becomes

$$\int \left[ \frac{1}{v} \left( \frac{\partial \eta}{\partial \epsilon} \delta \epsilon + \frac{\partial \eta}{\partial v} \delta v \right) - \frac{\eta}{v^2} \delta v \right] dS = 0$$

or, by (46),

$$\int \left\{ \left( \frac{p}{vT} - \frac{\eta}{v^2} \right) \delta v + \frac{1}{vT} \delta \epsilon \right\} dS = 0, \quad (56)$$

and this must be satisfied for all values of  $\delta v$  and  $\delta \epsilon$  which are compatible with the conditions

$$\delta \int \frac{1}{v} dS = 0 \text{ and } \delta \int \frac{1}{v} (\epsilon + \chi) dS = 0,$$

$$\text{i.e. with} \quad \int \frac{1}{v^2} \delta v dS = 0 \quad (57)$$

$$\text{and with} \quad \int \left\{ \frac{1}{v} \delta \epsilon - \frac{1}{v^2} (\epsilon + \chi) \delta v \right\} dS = 0. \quad (58)$$

Proceeding by a known mathematical method, we multiply (57) and (58) by factors  $C_1$  and  $C_2$  which are constant, *i.e.* the same for all volume-elements, add the results to (56), and equate the coefficients of  $\delta v$  and  $\delta \epsilon$  to zero.

Thus we find the equations \*

$$-\frac{\eta}{v^2} + \frac{p}{vT} + \frac{C_1}{v^2} - \frac{C_2}{v^2} (\epsilon + \chi) = 0$$

$$\text{and} \quad \frac{1}{vT} + \frac{C_2}{v} = 0.$$

By the latter equation the temperature must be the same throughout the body. Putting, therefore, in the former equation  $C_2 = -1/T$  and multiplying by  $Tv^2$ , we have

$$-\eta T + pv + \epsilon + \chi = -C_1 T,$$

and since  $C_1 T$  is constant, this is identical with (55b).

The equivalence of the two methods, based on  $\Psi$  and on  $\eta$ , is now manifest. This equivalence holds for all such problems.

\* If  $N$  is the number of elements  $dS$ , we have in (56)  $2N$  variations  $\delta v$  and  $\delta \epsilon$ . If all these could be chosen arbitrarily, the coefficient of each of them would be zero. Such, however, is not the case, since the variations are bound by (57) and (58), so that only  $2N - 2$  of them can be chosen arbitrarily. Eliminating between (56), (57), and (58) two of these variations, the first and the second, say, we should have an equation containing  $2N - 2$  variations only, and the coefficients of all these must be zero. Now, a convenient method of carrying out this elimination consists in adding up the three equations after having multiplied (57) by  $C_1$  and (58) by  $C_2$ . We may imagine that  $C_1$  and  $C_2$  were so chosen that the coefficients of the first and the second variations vanish; then the elimination is accomplished. With these values of  $C_1$  and  $C_2$  the remaining coefficients will then also vanish. Thus, with appropriately chosen values of  $C_1$  and  $C_2$  all coefficients will vanish.

It is worthy of especial notice that the problem of the equilibrium of a system can in general be treated by means of the free energy as well as by means of the entropy, and often also by means of the thermodynamical potential. The results must always be the same. The state of a body cannot depend, of course, upon the choice of the mathematical artifice. The same state of equilibrium has the property that under certain circumstances the variation of the free energy and under other circumstances that of the entropy vanishes.

This agreement of the results is perfectly intelligible, since the properties of entropy and free energy used in obtaining them were all derived from the second law of thermodynamics.

45. *Application to a system composed of liquid and vapour.*—In order to deduce the equilibrium condition for this system by means of the free energy we assume that the temperature is constant and that the walls of the containing vessel are fixed, so that no external work is being done.

Let the number of mass units contained in the first phase be  $n_1$ , the volume and the free energy per mass unit  $v_1$  and  $\Psi_1$ , and let  $n_2$ ,  $v_2$ ,  $\Psi_2$  have similar meanings for the second phase. In the state of equilibrium  $\Psi = n_1\Psi_1 + n_2\Psi_2$  must be a minimum and therefore,  $\delta(n_1\Psi_1 + n_2\Psi_2) = 0$  for all variations of  $n_1$ ,  $n_2$ ,  $v_1$ , and  $v_2$  satisfying the conditions

$$\begin{aligned}\delta(n_1 + n_2) &= 0, \\ \delta(n_1v_1 + n_2v_2) &= 0.\end{aligned}$$

From the first of these three equations follows

$$\Psi_1\delta n_1 + n_1\frac{\partial\Psi_1}{\partial v_1}\delta v_1 + \Psi_2\delta n_2 + n_2\frac{\partial\Psi_2}{\partial v_2}\delta v_2 = 0, \quad (59)$$

from the second,

$$\delta n_1 + \delta n_2 = 0 \text{ or } \delta n_2 = -\delta n_1,$$

and from the third,

$$\begin{aligned}v_1\delta n_1 + n_1\delta v_1 + v_2\delta n_2 + n_2\delta v_2 &= 0 \\ \text{or} \quad n_2\delta v_2 &= -n_1\delta v_1 - (v_1 - v_2)\delta n_1.\end{aligned}$$

The last two relations substituted in (59) give

$$\Psi_1\delta n_1 + n_1\frac{\partial\Psi_1}{\partial v_1}\delta v_1 - \Psi_2\delta n_1 - \frac{\partial\Psi_2}{\partial v_2}\{n_1\delta v_1 + (v_1 - v_2)\delta n_1\} = 0.$$



Since  $\delta v_1$  and  $\delta n_1$  are arbitrary, the conditions of equilibrium become

$$\frac{\partial \Psi_1}{\partial v_1} = \frac{\partial \Psi_2}{\partial v_2}, \text{ i.e. } p_1 = p_2. \quad (60)$$

and 
$$\Psi_1 - \Psi_2 - (v_1 - v_2) \frac{\partial \Psi_2}{\partial v_2} = 0,$$

or, by (60),

$$\Psi_1 - v_1 \frac{\partial \Psi_1}{\partial v_1} = \Psi_2 - v_2 \frac{\partial \Psi_2}{\partial v_2}, \text{ i.e. } \zeta_1 = \zeta_2.$$

Thus the pressure and the thermodynamical potential per unit mass must have the same values in both phases.

The same result can be obtained by means of the law of entropy. As independent variables will now be chosen for either phase (and per mass unit)  $\epsilon$  and  $v$ , and the volume will again be assumed constant. In the state of equilibrium  $n_1\eta_1 + n_2\eta_2$  will be a maximum for variations corresponding to the absence of heat supply, *i.e.* (since the volume is constant) to a constant energy. Thus, the equation to be satisfied is

$$\delta(n_1\eta_1 + n_2\eta_2) = 0$$

with the conditions

$$\delta(n_1 + n_2) = 0, \quad \delta(n_1v_1 + n_2v_2) = 0, \quad \delta(n_1\epsilon_1 + n_2\epsilon_2) = 0.$$

The remaining steps may be left to the reader.

The same problem can also be treated by means of the thermodynamical potential. The system will now be supposed to be kept, by means of a piston, at constant pressure, and at constant temperature. If  $\omega$  mass units pass from the phase 2 to the phase 1, the thermodynamical potential of the system changes by  $\omega(\zeta_1 - \zeta_2)$ . For equilibrium this change must be nil, so that

$$\zeta_1 = \zeta_2.$$

Now,  $\zeta_1 = f_1(p, T)$  and  $\zeta_2 = f_2(p, T)$ . Thus the equation  $\zeta_1 = \zeta_2$  amounts to a relation between  $p$  and  $T$ . Since, however,  $\zeta_1$  and  $\zeta_2$  can hardly be expressed as functions of  $p, T$ , we prefer to deduce from this equation another equation which will give the connection between the simultaneous changes of  $p$  and  $T$ . Let us assume that there is equilibrium for  $p, T$  and also for  $p + dp, T + dT$ , and let us compare these two states of equilibrium,

$$\begin{aligned} \zeta_1(T, p) &= \zeta_2(T, p), \\ \zeta_1(T + dT, p + dp) &= \zeta_2(T + dT, p + dp). \end{aligned} \quad (61)$$

By subtraction of these equations from each other we find

$$\frac{\partial \zeta_1}{\partial T} dT + \frac{\partial \zeta_1}{\partial p} dp = \frac{\partial \zeta_2}{\partial T} dT + \frac{\partial \zeta_2}{\partial p} dp,$$

whence, by (47),

$$\frac{dp}{dT} = \frac{\eta_1 - \eta_2}{v_1 - v_2}. \quad (62)$$

We have already found (Art. 26) Clapeyron's formula

$$\frac{dp}{dT} = \frac{r}{T(v_1 - v_2)}.$$

Clearly the two formulæ must coincide with each other, both being deduced from the second law. Their equivalence will become manifest by considering the passage of a mass unit from phase 2 to phase 1 at constant temperature and under equilibrium pressure. In fact, this process being reversible, formula (37) with the equality sign is applicable, and therefore,

$$\frac{r}{T} = \eta_1 - \eta_2.$$

46. Suppose now the substance can exist in three phases, 1, 2, and 3, viz. as a liquid, solid, and vapour. We then have for the equilibrium of liquid-vapour

$$\zeta_1 = \zeta_3,$$

and similarly for the equilibrium of the solid and the vapour phases

$$\zeta_2 = \zeta_3,$$

and for that of solid-liquid

$$\zeta_1 = \zeta_2.$$

As before for liquid and vapour we should now be able to deduce herefrom equations governing the change with temperature of the vapour pressure over a solid body and of the melting pressure.

If  $\zeta_1$ ,  $\zeta_2$ , and  $\zeta_3$  were known as functions of  $p$  and  $T$ , we could construct three curves representing the equilibrium between every two of the three phases. If now the temperature is such that the maximum vapour pressures over the liquid and over the solid are the same, the solid and the liquid phase can also be in equilibrium with each other. For, if  $\zeta_1 = \zeta_3$  and  $\zeta_2 = \zeta_3$ , we have also  $\zeta_1 = \zeta_2$ . Thus the three curves intersect in a point,

called *the triple point* (Fig. 9). Which of the three lines will be the steepest? To answer this question we have to take an

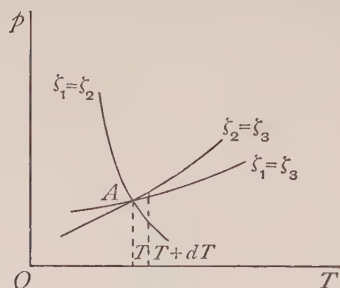


FIG. 9.

abscissa near the triple point and to see for which of the three lines the corresponding ordinate is the greatest. We have thus to consider the differences of the ordinates. Let the abscissa be  $T+dT$ , where  $T$  is the temperature of the triple point. To  $dT$  will then correspond three different  $dp$ 's which may be denoted by  $(dp)_{12}$ ,  $(dp)_{23}$ , and  $(dp)_{31}$ . Passing

from  $T$  to  $T+dT$  along the line  $\zeta_1 = \zeta_2$ , we have

$$\frac{\partial \zeta_1}{\partial T} dT + \frac{\partial \zeta_1}{\partial p} (dp)_{12} = \frac{\partial \zeta_2}{\partial T} dT + \frac{\partial \zeta_2}{\partial p} (dp)_{12}$$

or 
$$\left( \frac{\partial \zeta_1}{\partial T} - \frac{\partial \zeta_2}{\partial T} \right) dT + (v_1 - v_2) (dp)_{12} = 0,$$

and similarly, for the remaining two lines,

$$\left( \frac{\partial \zeta_2}{\partial T} - \frac{\partial \zeta_3}{\partial T} \right) dT + (v_2 - v_3) (dp)_{23} = 0,$$

$$\left( \frac{\partial \zeta_3}{\partial T} - \frac{\partial \zeta_1}{\partial T} \right) dT + (v_3 - v_1) (dp)_{31} = 0.$$

To eliminate  $dT$ , we add these equations. This gives

$$(v_1 - v_2) (dp)_{12} + (v_2 - v_3) (dp)_{23} + (v_3 - v_1) (dp)_{31} = 0,$$

or, if  $p_{12}$ ,  $p_{23}$ ,  $p_{31}$  be the ordinates themselves corresponding to the temperature  $T+dT$ , and if  $(v_2 - v_3)$  is replaced by  $(v_2 - v_1) + (v_1 - v_3)$ ,

$$(p_{12} - p_{23}) : (p_{31} - p_{23}) = (v_1 - v_3) : (v_1 - v_2). \quad (63)$$

Thus the ratio of the pressure differences is equal to that of the volume differences. Whence we readily see that the situation of the lines is as in Fig. 9. The line  $\zeta_1 = \zeta_3$  belongs to those two phases which most differ from each other in specific volume. These are in the case of water, to which the figure refers, the liquid and the vapour phase.

47. *Vapour pressure of solutions.*—For the system of a liquid and its vapour, considered in the preceding articles, the pressure is, at a given temperature, constant, no matter what

the volume. If the system is closed off by a piston to which a constant external pressure is applied, the equilibrium is neutral, *i.e.* independent of the position of the piston. The case is different when a solution of a substance, which itself does not evaporate, is in contact with the vapour of the solvent, let us say, water. The piston, subjected to a constant external pressure, is then in a stable equilibrium. If it is raised a little, some water evaporates but not so much as to keep the vapour pressure at its original height. In fact, owing to the increased concentration of the solution, the equilibrium pressure of the vapour is lowered.

In spite of this difference the condition of equilibrium can again be deduced in the same way from the theory of the thermodynamical potential. Let  $p$  be the pressure in the state of equilibrium which we will call  $A$ . We can then very well imagine other states, though not of equilibrium, in which at the same pressure  $p$  there is a little more or less water in the solution and as much less or more in the vapour phase. If such a state existed for a moment, the system would pass from it to the state  $A$ , and in this irreversible process the thermodynamical potential would diminish. Among all states possible at the pressure  $p$  the state  $A$  is characterised by a minimum of the thermodynamical potential, and the condition of equilibrium will, therefore, be obtained by equating to zero the change of this potential for an infinitesimal change of the system starting from  $A$ .

Let us work out this problem. The state of the solution can be determined by its "concentration" or "dilution", the former being the quantity of the dissolved substance per unit weight of the solvent, and the latter, which we will use, the quantity  $k$  of the solvent per unit weight of the solute. The thermodynamical potential of the solution per unit weight of the dissolved substance will be denoted by  $\zeta$ . This will be a function of  $p$ ,  $T$ , and  $k$ . Further,  $\zeta_1$  will stand for the thermodynamical potential of the pure solvent, at the said pressure  $p$  and temperature  $T$ , and  $\zeta_2$  for that of the vapour, both per unit weight.

If  $m$  be the total weight of the solute, the thermodynamical potential of the solution is  $m\zeta$ .

Now, if an infinitesimal quantity  $\delta$  of the solvent evaporates

from the solution, the thermodynamical potential of the vapour increases by  $\zeta_2\delta$ , and since  $k$  diminishes by  $\delta/m$ , the change of the thermodynamical potential of the solution will be  $-\frac{\partial\zeta}{\partial k}\delta$ .

Hence, the condition of equilibrium,

$$\zeta_2 = \frac{\partial\zeta}{\partial k}. \quad (64)$$

This equation is, ultimately, a relation between  $p$ ,  $T$ , and  $k$ . At first sight not much can be done with it, but we can deduce from it a relation between simultaneous *changes* of  $k$  and  $p$ . If the temperature be kept constant,  $\zeta_2$  will depend only on  $p$ , and  $\zeta$  on  $p$  and  $k$ , and (64) will give

$$\frac{\partial\zeta_2}{\partial p}dp = \frac{\partial^2\zeta}{\partial k\partial p}dp + \frac{\partial^2\zeta}{\partial k^2}dk. \quad (65)$$

What is the meaning of the coefficients in this equation? The first,  $\partial\zeta_2/\partial p$ , is, by (47), the volume,  $v_2$  say, of a weight unit of saturated vapour in contact with the solution. Again,  $\partial\zeta/\partial p$  is the volume of a quantity of solution containing one part of the solute and  $k$  parts of the solvent, and  $\frac{\partial^2\zeta}{\partial k\partial p} = \frac{\partial v}{\partial k}$  is the change

of that volume due to the addition of a small quantity  $dk$  of solvent, per unit weight of added solvent. If there were no contraction due to dilution,  $\partial^2\zeta/\partial k\partial p$  would be the volume of unit weight of the solvent, at the given  $p$  and  $T$ .

Equation (65) now becomes

$$\left(v_2 - \frac{\partial v}{\partial k}\right)dp = \frac{\partial^2\zeta}{\partial k^2}dk.$$

This formula enables us to determine the change of pressure  $dp$  produced by a given change  $dk$  of the dilution. Since  $v_2 - \frac{\partial v}{\partial k}$  and (for reasons which will appear later) also  $\partial^2\zeta/\partial k^2$  is positive, it follows that the vapour pressure increases with the dilution of the solution.

48. In order to find, for a given temperature, the difference in vapour pressure over pure water and over a solution of dilution  $k$  it will be best to return to (64). This equation or, more explicitly,

$$\zeta_{2(p)} = \frac{\partial\zeta}{\partial k_{(p)}}, \quad (66)$$

determines the vapour pressure  $p$  of the solution at a given temperature  $T$ . On the other hand, the vapour pressure  $p_0$  of pure water is given by

$$\zeta_{2(p_0)} = \zeta_{1(p_0)}, \quad \dots \quad (67)$$

which actually is a sub-case of (66). In fact, it follows from the meaning of  $\partial\zeta/\partial k$  that its value tends with increasing  $k$  to  $\zeta_1$ .

From (66) and (67) we have

$$\zeta_{2(p)} - \zeta_{2(p_0)} = \frac{\partial\zeta}{\partial k(p)} - \zeta_{1(p_0)}. \quad \dots \quad (68)$$

Now, at constant temperature,  $\frac{\partial\zeta_2}{\partial p} = v_2$ . Thus the left-hand member is equal to  $\int_{p_0}^p v_2 dp$ . If, further, Boyle's law is assumed to hold for the vapour,  $v_2 = RT/p$ , and formula (68) becomes

$$RT \log \frac{p}{p_0} = \frac{\partial\zeta}{\partial k(p)} - \zeta_{1(p_0)}. \quad \dots \quad (69)$$

Differentiating this with respect to temperature we will have an equation between the vapour pressure on the one hand and a quantity of heat on the other hand, analogous with the formula (35) for the vapour pressure of a simple substance. With regard to this differentiation it will be kept in mind that the independent variables in (69) are  $k$  and  $T$ . The pressure  $p$  depends on both these variables, while  $p_0$  depends on  $T$  alone. Thus, keeping  $k$  constant and differentiating with respect to temperature,  $p_0$  and  $p$  must also be varied. The process amounts to writing down (69) for two indefinitely near temperatures and subtracting the two equations from each other.

The result is

$$R \frac{d}{dT} \left( T \log \frac{p}{p_0} \right) = \frac{\partial^2\zeta}{\partial k \partial T(p)} + \frac{\partial^2\zeta}{\partial k \partial p(p)} \frac{dp}{dT} - \frac{\partial\zeta_1}{\partial T(p_0)} - \frac{\partial\zeta_1}{\partial p(p_0)} \frac{dp_0}{dT}. \quad (70)$$

Here the second and the fourth term of the right-hand member can be omitted. In fact,  $\frac{\partial\zeta_1}{\partial p} = v_1$  is the volume of unit weight

of the solvent, while  $\frac{\partial\zeta}{\partial p} = v$ , and therefore,  $\frac{\partial^2\zeta}{\partial k \partial p} = \frac{\partial v}{\partial k}$ , which is

of the same order as  $v_1$ . Developing the left-hand member, we have  $dp/dT$  and  $dp_0/dT$  multiplied by  $RT/p$  and  $RT/p_0$ , and these two expressions represent the volume of unit weight of vapour



under the pressures  $p$  and  $p_0$  respectively, and are thus much greater than  $v_1$ . Therefore,

$$R \frac{d}{dT} \left( T \log \frac{p}{p_0} \right) = \frac{\partial^2 \zeta}{\partial k \partial T_{(p)}} - \frac{\partial \zeta_1}{\partial T_{(p_0)}}. \quad (71)$$

Now, it will be remembered (p. 50) that the heat generated, when a system at constant pressure  $p$  passes from one state  $A$  to another  $B$ , is given by the decrease of the function

$$\zeta - T \frac{\partial \zeta}{\partial T},$$

which for brevity will be denoted by  $\chi$ . This symbol will in particular be used for the aforesaid quantity of the solution,\* while  $\chi_1$  will be referred to a unit of the solvent. Thus, multiplying (71) by  $T$  and subtracting (69),

$$RT^2 \frac{d}{dT} \log \frac{p}{p_0} = \chi_{1(p_0)} - \frac{\partial \chi}{\partial k_{(p)}},$$

where, finally,  $\chi_{1(p_0)}$  is to be replaced by  $\chi_{1(p)}$ . Ultimately, therefore, the equation becomes

$$RT^2 \frac{d}{dT} \log \frac{p}{p_0} = Q, \quad (72)$$

where

$$Q = \chi_{1(p)} - \frac{\partial \chi}{\partial k_{(p)}}.$$

As to the meaning of the right-hand member of (72),  $Qdk$  represents the generation of heat which takes place when an infinitesimal quantity of water  $dk$  under the pressure  $p$  is added to a quantity of the solution containing a unit of the solute, the solution itself being before and after this addition under the same pressure. In fact, the generated heat is equal to the decrement of the function  $\chi$ , for the whole system, due to the addition of water. Now, before the dilution we have  $\chi_1 dk$  for the water and  $\chi$  for the solution, and after the dilution,  $\chi + \frac{\partial \chi}{\partial k} dk$  for the solution. Thus the diminution of the total  $\chi$  is

$$\left( \chi_1 - \frac{\partial \chi}{\partial k} \right) dk = Qdk.$$

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\* I.e. per unit weight of dissolved substance.

The well-known formula (72) was found many years ago by Kirchhoff by an entirely different method. The terms neglected in the right-hand member are : first,

$$T\left(\frac{\partial v}{\partial k}\frac{\partial p}{\partial T}-v_1\frac{\partial p_0}{\partial T}\right),$$

consisting of the magnitudes omitted in (70), and, second,  $\chi_{1(p_0)} - \chi_{1(p)}$ , which can be written

$$(p_0 - p)\frac{\partial \chi_1}{\partial p},$$

or, remembering the meaning of  $\chi_1$ ,

$$(p_0 - p)\left(v_1 - T\frac{\partial v_1}{\partial T}\right).$$

Kirchhoff's formula holds only when the principal term of this expression, viz.  $(p_0 - p)v_1$ , is small compared with the heat  $Q$ .

49. *Mixtures*.—We shall thus call mixtures in the usual sense of the word as well as solutions, and it will be understood once for all that they are taken at constant temperature and pressure. In order to find their equilibrium conditions use will be made of the thermodynamical potential which, as we already know, cannot increase in processes at constant temperature and pressure. We will also avail ourselves of appropriate graphical representations which will make the matter more clear and will enable us to answer a number of questions almost without calculation.

We will limit ourselves to the case of two or three components, and each of these will be expressed in gram molecules as units. If the mixture, whether homogeneous or not, contains  $m_1$  and  $m_2$ , or  $m_1$ ,  $m_2$ , and  $m_3$  gram molecules of the components, we will say that we have in all  $m_1 + m_2$  or  $m_1 + m_2 + m_3$  gram molecules. It will be assumed throughout that we have to do with a gram molecule of mixture, so that the sum  $m_1 + m_2$  or  $m_1 + m_2 + m_3$  will always be equal to unity.

50. *Two components*.—We will first consider the case of two components. We put  $m_2 = x$  and  $m_1 = 1 - x$ , and we cut off the values of  $x$  and  $\zeta$  on two mutually perpendicular co-ordinate axes as abscissa and ordinate respectively. We choose the

additive constant in  $\zeta$  so great that the value of  $\zeta$  for the mixture

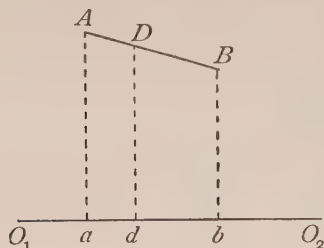


FIG. 10.

should always be positive. The system for which  $x=O_1a$  and  $\zeta=aA$  (cf. Fig. 10) will be called the system or the mixture  $A$ , and the point  $A$  the  $\zeta$ -point of the system. If now  $\mu$  gram molecules of the mixture  $A$  are put together with  $1-\mu$  gram molecules of the mixture  $B$ , the point  $d$  representing the composition of

the resulting system is so placed between  $a$  and  $b$  that

$$ad : bd = (1 - \mu) : \mu. \quad (73)$$

In other words,  $d$  is the centre of gravity of two particles of masses  $\mu$  and  $1-\mu$  placed at  $a$  and  $b$ . This follows directly by noticing that according to (73)

$$O_1d = \mu \cdot O_1a + (1 - \mu) \cdot O_1b,$$

which shows that the quantity of the second component ( $m_2$ ) in the whole system is indeed given by the length  $O_1d$ .

*Vice versa*, as regards the quantities of the components, a system whose composition is represented by  $d$  can always be split into two systems represented by  $a$  and  $b$ , a gram molecule of  $d$  giving  $bd/ab$  gram molecules of  $a$  and  $ad/ab$  gram molecules of  $b$ .

Let us still notice that if  $\mu$  gram molecules of  $a$  are put together with  $1-\mu$  gram molecules of  $b$  without changing their state, so that they do not mix with each other but form a "complex" ( $a,b$ ), the thermodynamical potential of this complex will be represented by the segment  $dD$  cut off the vertical line by the join  $AB$ . In fact,

$$dD = \mu \cdot aA + (1 - \mu) \cdot bB.$$

Thus the point  $D$ , the  $\zeta$ -point of the complex  $\{\mu a, (1-\mu)b\}$ , lies on the join  $AB$  so that  $AD : BD = (1-\mu) : \mu$ ; it coincides with the centre of gravity of two masses  $\mu$  and  $1-\mu$  placed at  $A$  and  $B$ .

The quantities of the components contained in the complex  $D$  may also occur in other states, as *e.g.* if they form a homogeneous mixture or are differently distributed over the several phases than in the complex under consideration. The point repre-

sending the composition is then still  $d$ , but the  $\zeta$ -point can lie above or below  $D$ .

Let us suppose that the two components occur in the liquid state and can mix with each other in all proportions, so that  $x$  can vary from 0 to 1. Then the  $\zeta$ -points of the liquid phases will lie on a curve (Fig. 11) whose initial and end-ordinate for the values 0 and 1 of  $x$  are given by the thermodynamical potentials of the pure liquid components ( $O_1P$  and  $O_2Q$ ).<sup>\*</sup> If this curve is known, the thermodynamical potential of a non-mixed complex can be determined by means of the theorems just proved. The question is whether such a complex can remain unmixed or will change into a homogeneous mixture.

51. *Stable and unstable liquid phases; equilibrium between two liquid phases.*—If the  $\zeta$ -curve is convex towards the  $x$ -axis at a point  $A$  (Fig. 11), then  $A$  lies below the chord which joins two points of the curve ( $A'$  and  $A''$ , not marked in the figure) taken on both sides of and at a small distance from  $A$ . In this case, therefore, the thermodynamical potential has a smaller value for the homogeneous mixture than for the unmixed complex ( $A'$ ,  $A''$ ). Thus, if the phases  $A'$  and  $A''$  are brought together, they can mix, under diminution of the thermodynamical

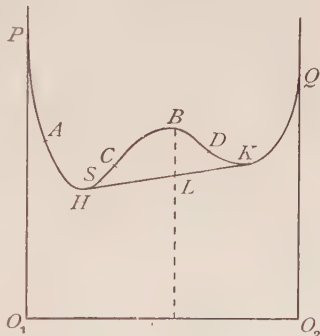


FIG. 11.

potential, into a homogeneous phase  $A$ , whereas the latter cannot split into two phases  $A'$  and  $A''$ , since this would be accompanied by an increase of the thermodynamical potential, which is impossible. Let us now consider a point  $B$  where the  $\zeta$ -curve turns towards the  $x$ -axis its concave side. If  $B'$  and  $B''$  are again two points on both sides of and near to  $B$ , then  $B$  lies above the join  $B'B''$ , whence we conclude that the phases  $B'$  and  $B''$  will not tend to form a homogeneous mixture; on the other hand,  $B$  can split, under diminution of the thermodynamical potential, into the phases  $B'$  and  $B''$ .

<sup>\*</sup> A discussion of systems in which one component is present in a very small quantity would show that the  $\zeta$ -curve slopes down starting from  $P$ , rises towards  $Q$ , and is tangential at  $P$  and  $Q$  to the lines  $O_1P$  and  $O_2Q$ .

The equilibrium in a state such as  $A$  is called stable, and in a state such as  $B$ , unstable.

It remains to be seen whether the thermodynamical potential, whenever it can diminish, does actually diminish. From what we know, such will commonly be the case, at least if the transition consists of a continuous series of changes of state; if, however, in order to pass from one state to another a jump is necessary, the transition does not take place (supersaturation, superfusion).

From these considerations we see that if a stable liquid phase is to be possible for each value of  $x$ , the  $\zeta$ -curve must turn its convex side everywhere downwards or  $\partial^2\zeta/\partial x^2$  must be positive for every value of  $x$ .\* If a part of the  $\zeta$ -curve turns its concave side downwards, so that  $\partial^2\zeta/\partial x^2$  is negative, the corresponding phases are unstable; they cannot be produced by bringing together the liquid components. The latter case is assumed in Fig. 11 and occurs, *e.g.*, for water and ether. If these liquids are put together, they form two layers of which one contains much water and the other much ether. In a case like this the  $\zeta$ -curve has two inflexion points,  $C$  and  $D$ . A point of the line  $CBD$  cannot be realised, since a mixture such as  $B$  would at once split into two phases  $B'$  and  $B''$ , infinitely near  $B$ ; each of these will again split into two other phases, and this process will go on until stability is reached, which, as will be seen, will be attained only in  $L$ , a point of the straight line  $HK$  tangential to the curve at  $H$  and  $K$ . For the parts  $PC$  and  $QD$  holds good what was said at the beginning of this article. They represent stable equilibria, while the states between  $C$  and  $D$ , which might be possible according to the molecular theory, appear here as states of unstable equilibrium. Further, all complexes represented by points of the double tangent  $HK$  between  $H$  and  $K$  are readily seen to be possible; in fact, there is then no transformation in which the thermodynamical potential could decrease. Thus,  $H$  and  $K$  represent two liquid phases which can be in equilibrium with each other.

But what about points such as  $S$  which lie between the point of contact  $H$  and the inflexion point  $C$ ? A mixture corresponding to such a point can transform itself, with decreasing thermodynamical potential, into a complex of the states [phases]

\* By a similar reasoning it will be seen that in the case treated on p. 66  $\partial^2\zeta/\partial k^2$  is positive, if the solution is stable for every value of the dilution  $k$ .

$H$  and  $K$ . Yet, while the state  $S$  can gradually pass into  $H$ , the state  $K$  cannot be reached without a jump, which the substance, as it seems, does not make. The presence, however, of a small quantity of the phase  $K$  is then sufficient to transform that jump into a continuous change. In fact, if we imagine  $K$  connected with all points of the curve from  $S$  to  $H$  (Fig. 12),



FIG. 12.

then, while the substance passes through all the states from  $S$  through  $S'$  down to  $S''$ , the quantity of the substance  $K$  already present will change but gradually.

Thus, points between the inflexion point and the point of contact represent states of little stability; all the most stable states are represented by the curve  $PH$ , the straight line  $HK$ , and the curve  $KQ$  (Fig. 11).

52. *Equilibrium between a solid and a liquid phase, superfusion.*—Such states which in themselves are stable, but at a slight disturbance change into

a more stable complex, are principally known in connection with solutions. Of this kind is the phenomenon of supersaturation. Let  $Z_2$  (Fig. 13) be the thermodynamical potential, per gram molecule, of the solid,  $Z_1$  that of the liquid salt,  $W$  that of water, and let the curve  $Z_1W$  represent the potentials of all thinkable solutions, all taken, of course, at the same temperature and pressure. In this case the tangent  $Z_2A$

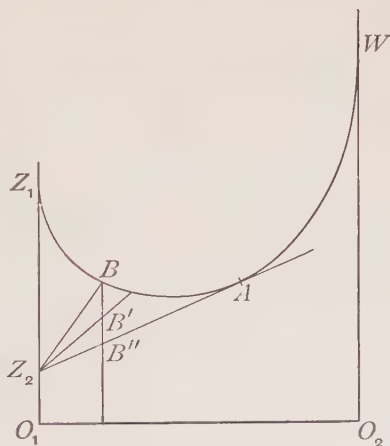


FIG. 13.

plays a rôle similar to the double tangent  $HK$  in the preceding case, and the states between  $A$  and  $Z_1$  correspond to



those between  $H$  and  $C$  in Fig. 11. Let us imagine, for example, a solution in the state  $B$ . In itself it is stable, since its thermodynamical potential cannot be diminished by a continuous change of this state. But in the presence of ever so small a quantity of solid salt (state  $Z_2$ ) the solution will at once pass successively through the states  $B'$ , etc., until stable equilibrium is attained in  $B''$ , the intersection point of the ordinate of  $B$  and the tangent  $Z_2A$ . The final result is a complex corresponding to this point.

At first sight it would seem impossible to speak of the thermodynamical potential of a system consisting of solid and of melted salt at the same temperature unless the two phases are in mutual equilibrium, as they are at the melting point only. But as water can be cooled far below  $0^\circ$  C. without freezing, provided it is not in contact with ice, so also can melted salt exist, in absence of solid salt, below the melting temperature. The reason for placing  $Z_2$  below  $Z_1$  is that a substance in the state of superfusion solidifies as soon as it is brought into contact with the solid phase, and this must be accompanied by a decrease of the thermodynamical potential.

A complex consisting of superfused salt and a minute quantity of solid salt is represented by a point placed a little below  $Z_1$ , whence it passes gradually to  $Z_2$ . Fig. 13, of course, is drawn for temperatures below the melting point. For the melting temperature  $Z_1$  and  $Z_2$  coincide, and for higher temperatures  $Z_2$  lies above  $Z_1$ . In the latter case the solid is in a state of supergelation, its melting being delayed. The form and the position of the curve will, besides, be different for different temperatures.

All these considerations will be seen to depend upon the manner in which the thermodynamical potential of a complex of two substances is determined from the thermodynamical potentials of these substances and the composition of the complex.

53. *Equilibrium of three phases consisting of two components.*—Such an equilibrium cannot exist for arbitrary values of  $p$  and  $T$ . If, however, the temperature is kept fixed and the pressure is lowered or raised, the figure undergoes a gradual change, and when the pressure has attained a certain value, the  $\zeta$ -point of a solid phase may happen to lie on the double tangent of the  $\zeta$ -curve for the liquid phases. In this case the solid phase can be in equilibrium with two liquid mixtures.

Again, at an arbitrary temperature but only under a certain pressure depending upon it, two solid phases can coexist with a liquid one: if such is to be the case, the join of the  $\zeta$ -points representing the two solid phases must be tangential to the  $\zeta$ -curve.

It will also be readily seen that at a determined temperature and a determined pressure two solid and two liquid phases can be in equilibrium with each other. This will be confirmed later on in another way.

54. *Equilibrium of salt solutions with solid hydrates.*—The thermodynamical potential for all possible solutions of a salt in water (always per gram molecule of solution) is again given by a curve (Fig. 14).

We can also represent the potential for a gram molecule of the solid hydrate by an ordinate erected at a point of the axis  $O_1O_2$  whose abscissa determines the composition of the hydrate ( $x$  being the quantity of water and  $1-x$  that of water-free salt). Now, if  $A$  be the  $\zeta$ -point of the solid hydrate, two tangents can in general

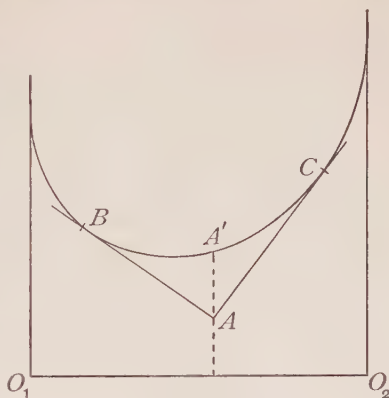


FIG. 14.

be drawn from it to the curve, that is to say, the hydrate can be in equilibrium with two solutions, one containing more and the other less water than the hydrate. A solution represented by a point of the curve placed between the points of contact  $B$  and  $C$  cannot be in equilibrium with the solid hydrate.  $A'$  is the  $\zeta$ -point of liquid hydrate which, when a little solid hydrate is added, will at once pass entirely into the solid state.

If we now imagine the figure drawn for other temperatures, the point  $A$  may fall upon the curve. This will be the case for the temperature of melting, when the liquid and the solid hydrates are in equilibrium with each other.

55. Let us now take up the case of Fig. 15, in which a part of the  $\zeta$ -curve turns its concave side downwards, so that we can have equilibrium between two solutions of different concentration.

Consider a solid substance in a water-free state, represented by the  $\zeta$ -point  $A$ . From  $A$  can be drawn two tangents to the curve

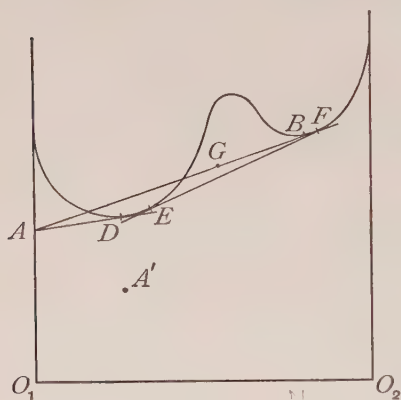


FIG. 15.

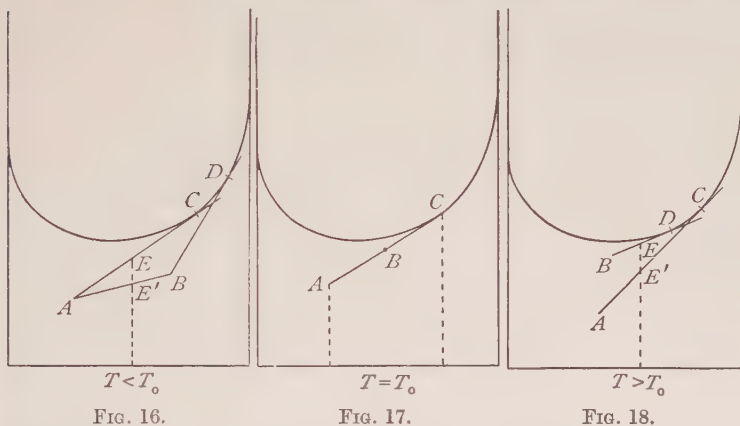
with points of contact on the stable part, and a third one (not shown in the figure) with a point of contact on the unstable part. Thus we have two different solutions which can be in equilibrium with the solid substance. As appears from the figure, a complex  $G$  consisting of a solid substance  $A$  and a solution  $B$  can transform itself, with decreasing  $\zeta$ , into a complex of two solutions  $E$  and  $F$ , if  $EF$  be a double

tangent. If the solid substance is not water-free, but a hydrate ( $\zeta$ -point  $A'$ ), it can be in equilibrium with three different solutions.

Next, suppose two hydrates of the same substance and of different water content were possible. Let their  $\zeta$ -points be  $A$  and  $B$  (Fig. 16). From these points draw the tangents  $AC$  and  $BD$  to the curve which we will now suppose to be wholly convex downwards. Then a solution to the right of  $D$  cannot be in equilibrium with the two hydrates, one at  $D$  can be in equilibrium with  $B$  alone, but then the solution is not yet super-saturated with respect to the less diluted hydrate  $A$ . There is thus nothing absolute about saturation. Points between  $C$  and  $D$  represent solutions which are non-saturated with respect to one hydrate,  $A$ , but supersaturated with respect to the other,  $B$ . This can, *e.g.*, be observed on sodium sulphate, namely, with the water-free salt and the hydrate containing 10 water molecules.

56. We will next investigate the changes of a system of two hydrates with temperature. At a certain temperature  $T_0$  the join of the corresponding two points  $A$  and  $B$  can be a tangent of the curve (Fig. 17). At this temperature, called transition temperature, there is then equilibrium between the two hydrates and a solution. By determining for each temperature the  $x$ -value of the solution, which is in equilibrium with the first

hydrate, a solubility curve can be constructed with  $T$  and  $x$  as co-ordinates measured along a pair of perpendicular axes. Similarly for the second hydrate. At the transition temperature the two solubility curves will intersect each other. If the most stable states only are considered, the solubility curve is a broken line consisting of two straight lines. In fact, since the thermodynamical potential tends to become as small as possible, the equilibrium with one hydrate is always more stable than that



with the other; only at the transition temperature are both equally stable.

For temperatures below the transition temperature the case of Fig. 16, and for temperatures above  $T_0$  that of Fig. 18, may occur.

For  $T < T_0$  the most stable states lie on the lines  $AB$  and  $BD$ , corresponding to complexes for which  $x$  is contained between the abscissæ of  $A$  and of  $D$ . The passage from  $E$  to  $E'$  may fail to take place, but not if some trace of the second hydrate  $B$  is present. In the latter case, then, a solid mixture of the two hydrates is formed.

For  $T > T_0$  (Fig. 18) the most stable states are represented by the points of the line  $AC$ . A complex  $E$ , consisting of the second hydrate  $B$  and a solution  $D$ , will transform itself into  $E'$  (complex of first hydrate and solution  $C$ ), provided there is a trace of the first hydrate. Otherwise the change may not take place.

A variety of other complicated cases may occur, according to the form of the curve and the position of the  $\zeta$ -points of the two hydrates.

57. The graphical representation can also be arranged in a somewhat different way. Thus, for instance, let the solution contain a weight unit of the substance  $A$  and  $x$  units of water. The diagrams can then be constructed and the conclusions drawn from them as before. But the figures will no longer be limited in the direction of  $x$ , since pure water will correspond to  $x = \infty$ . And the  $\zeta$ -curve will ascend beyond all limits, since the thermodynamical potential of an infinite quantity of water is infinite.

We may also proceed more generally.

Let the quantity of the substance  $A$  be denoted by  $a_1 + a_2x$ , and that of  $B$  by  $\beta_1 + \beta_2x$ , where the  $a$ 's and the  $\beta$ 's are arbitrary constants. Against  $x$  as abscissa we plot as ordinate the thermodynamical potential of the whole system obtained by putting together these quantities, which may now be called a "unit" of the mixture. If there is, besides, a solid phase, a homogeneous liquid one, etc., we shall have for each of them a  $\zeta$ -point.

The two methods previously considered can be deduced from this more general one. In the first of those methods the quantities of  $A$  and  $B$  were  $1 - x$  and  $x$  respectively, and in the second, 1 and  $x$ . Let us form, by the general method, a complex of two phases characterised by  $x$  and  $x'$ , and let this complex contain  $y$  units of the first and  $1 - y$  units of the second phase. The composition of the whole complex and its  $\zeta$ -point will then be derived from those of the constituent parts in exactly the same way as by the first method (p. 70).

In fact, the composition ( $x''$ ) of the complex will be given by

$$y(a_1 + a_2x) + (1 - y)(a_1 + a_2x') = a_1 + a_2x'',$$

which expresses the quantity of the substance  $A$ , or

$$yx + (1 - y)x' = x''.$$

Thus the point  $x''$  divides again the distance of the points  $x$  and  $x'$  in the ratio of  $1 - y$  to  $y$  and lies between  $x$  and  $x'$ . The proof for the  $\zeta$ -point may be left to the reader.

For  $x = -a_1/a_2$  the quantity of the first substance is nil, and for  $x = -\beta_1/\beta_2$  that of the second.



Thus the curve extends between the ordinates corresponding to these abscissæ.

### 58. *Three components.*

Let us now consider a mixture of three components. In order to represent in this case the composition and the thermodynamical potential of the mixture by the position of a point, we have to avail ourselves of a three-dimensional construction. Instead of the previous base line (for two components) we now take a fundamental plane which we may imagine to be horizontal. The quantity of the mixture will again be assumed to be always a gram molecule, so that  $m_1 + m_2 + m_3 = 1$ . Owing to this relation the composition of each phase or complex of phases will be determined by two variables and can thus be represented by the position of a point on the plane. This can be done in a variety of ways. We will take for  $m_1$ ,  $m_2$ , and  $m_3$  linear functions of the co-ordinates  $x$  and  $y$  of the point in question, so that also conversely  $x$  and  $y$  will be linear functions of  $m_1$ ,  $m_2$ ,  $m_3$ .

If now the points  $a$  and  $b$  of the fundamental plane (Fig. 19) correspond to two phases or complexes of phases, and if  $\mu$  gram molecules of the first are put together with  $1 - \mu$  gram molecules of the second, the composition of the new complex will be represented by a point  $d$  of the join  $ab$ , viz. by the centre of gravity of two masses  $\mu$  and  $1 - \mu$  placed at  $a$  and  $b$ , so that

$$ad : bd = (1 - \mu) : \mu.$$

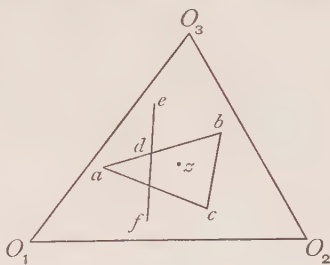


FIG. 19.

In fact, since  $x$  and  $y$  are linear functions of  $m_1$ ,  $m_2$ ,  $m_3$ , the co-ordinates of the point  $d$  representing the new complex will be, in terms of the co-ordinates of  $a$  and  $b$ ,

$$x_d = \mu x_a + (1 - \mu)x_b, \text{ etc.}$$

*Vice versa*, a system whose composition is represented by the point  $d$  can be split into two systems  $a$  and  $b$ , where  $a$  and  $b$  can be taken at any distance from  $d$ . Nor is this limited to a single line  $ab$ . If we draw through  $d$  any other line and take



upon it two points  $e$  and  $f$  on both sides of  $d$ , the system  $d$  can also be split into the systems  $e$  and  $f$ .

59. Next, let us consider three phases or complexes of phases  $a$ ,  $b$ ,  $c$ , of which  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  gram molecules are put together, so that  $\mu_a + \mu_b + \mu_c = 1$ . Owing to the linear relations between the co-ordinates and the quantities  $m$  the point representing the composition of the resulting system will have the co-ordinates

$$\mu_a x_a + \mu_b x_b + \mu_c x_c \text{ and } \mu_a y_a + \mu_b y_b + \mu_c y_c,$$

and will thus coincide with the centre of gravity of three masses  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  placed at  $a$ ,  $b$ , and  $c$ .

Whence it follows that all systems which can be composed of  $a$ ,  $b$ , and  $c$  have their representative points within, or on the perimeter of, the triangle  $abc$  of the fundamental plane. Conversely, if  $z$  is any point within this triangle, the system  $z$  can split in a perfectly definite way into the three systems  $a$ ,  $b$ ,  $c$ .

Three fixed points  $O_1$ ,  $O_2$ ,  $O_3$  of the fundamental plane will, in accordance with the assumed relations between  $m_1$ ,  $m_2$ ,  $m_3$  and the co-ordinates, correspond to the three components in a pure state. Thus the graphical representation will be confined to the triangle  $O_1 O_2 O_3$  in that plane.\*

What will be the form of the locus of the  $\zeta$ -points, the “ $\zeta$ -surface”?

These points will be obtained in much the same way as in the case of two components, viz. by drawing from each point of the fundamental plane within the triangle  $O_1 O_2 O_3$  a perpendicular, and cutting off the value of the thermodynamical potential of the corresponding system. (The points of the fundamental plane will be denoted by small letters, and the  $\zeta$ -points by capitals.) That the  $\zeta$ -point of a complex, consisting of  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  gram molecules of three systems whose  $\zeta$ -points are  $A$ ,  $B$ ,  $C$  (where  $\sum \mu = 1$ ), will coincide with the centre of gravity of the masses  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  placed at  $A$ ,  $B$ ,  $C$ , will now be obvious. All complexes consisting of two systems  $A$  and  $B$  have their  $\zeta$ -points on the join  $AB$ , and all those consisting of three systems  $A$ ,  $B$ ,  $C$  have their  $\zeta$ -points in the plane  $ABC$ . Finally, the

\* It can be proved that, in the case of two components, the  $\zeta$ -curve must be tangential to the limiting lines perpendicular to the  $x$ -axis. Similarly will the  $\zeta$ -surface for three components be tangential to the vertical planes laid through every two of the points  $O_1$ ,  $O_2$ ,  $O_3$ .

$\xi$ -points of two systems of the same composition lie on the same vertical line, and the possibility of transformation of one system into another depends only on the question which of these points lies lower.

60. The form of the  $\zeta$ -surface will be different, according as the homogeneous liquid phases of every composition are in stable equilibrium or not. If a phase  $D$  is in stable equilibrium, then all sections of the  $\zeta$ -surface by vertical planes through  $D$  must turn their convex sides downwards. If some of these sections are concave downwards, the phase  $D$  must be considered as unstable, since in this case the thermodynamical potential can diminish when this phase splits into two others; the points of the fundamental plane corresponding to these two phases will lie upon some straight line passing through the projection of  $D$  upon that plane.

An equivalent form of the condition of stable equilibrium is that the  $\zeta$ -surface in the neighbourhood of the given point  $D$  shall lie entirely above the tangential plane at that point. If homogeneous phases of every composition are stable, this condition must be satisfied at every point of the  $\zeta$ -surface, and the surface cannot have a "plait". Let  $x, y, \zeta$  be the co-ordinates of the point  $D$ , and  $x + \Delta x, y + \Delta y, \zeta + \Delta \zeta$  those of a neighbour point  $E$  of the  $\zeta$ -surface. Further, let  $\zeta + \Delta' \zeta$  be the ordinate of  $E'$ , the intersection point of the vertical line erected at  $E$  with the tangential plane at  $D$ . Then, up to terms of the third order in  $\Delta x$  and  $\Delta y$ ,

$$\Delta \zeta = \frac{\partial \zeta}{\partial x} \Delta x + \frac{\partial \zeta}{\partial y} \Delta y + \frac{1}{2} \frac{\partial^2 \zeta}{\partial x^2} \Delta x^2 + \frac{\partial^2 \zeta}{\partial x \partial y} \Delta x \Delta y + \frac{1}{2} \frac{\partial^2 \zeta}{\partial y^2} \Delta y^2$$

and

$$\Delta' \zeta = \frac{\partial \zeta}{\partial x} \Delta x + \frac{\partial \zeta}{\partial y} \Delta y.$$

Now, the conditions that  $E$  shall lie above  $E'$ , *i.e.* that the difference  $\Delta \zeta - \Delta' \zeta$  shall be positive for all values of  $\Delta x$  and  $\Delta y$ , are

$$\frac{\partial^2 \zeta}{\partial x^2} > 0, \frac{\partial^2 \zeta}{\partial y^2} > 0, \frac{\partial^2 \zeta}{\partial x^2} \frac{\partial^2 \zeta}{\partial y^2} > \left( \frac{\partial^2 \zeta}{\partial x \partial y} \right)^2,$$

of which the first or the second is, by the way, a consequence of the remaining two.

The curve determined by the equation

$$\frac{\partial^2 \zeta}{\partial x^2} \frac{\partial^2 \zeta}{\partial y^2} - \left( \frac{\partial^2 \zeta}{\partial x \partial y} \right)^2 = 0$$

is called the spinodal line. It divides the region of stable phases from that of unstable phases.

If in a part of the  $\zeta$ -surface the stability conditions are not satisfied, so that at least some vertical sections are concave downwards, the surface will have a plait. Such a plait can extend to one or two of the boundary curves, but it may as well be confined to the middle of the surface.

61. For any vertical section of the  $\zeta$ -surface all our previous considerations will be valid. Thus, a solid phase  $F$  will be in equilibrium with a liquid phase  $G$  if the join  $FG$  is tangential to the  $\zeta$ -surface. In the present case this condition will be satisfied for an infinity of liquid phases, viz. all those whose  $\zeta$ -point lies on the curve along which the cone with  $F$  as vertex touches the surface. Let this be a closed line.

Points of the  $\zeta$ -surface outside this curve of contact represent phases which cannot be in equilibrium with the solid phase; the solution is here either too much or not enough concentrated. The part of the surface inside the curve of contact corresponds to phases of little stability which in the presence of a trace of the solid phase will split.

The whole surface representing states in which the thermodynamical potential is as small as is possible under the given circumstances consists of the cone and of the  $\zeta$ -surface outside the curve of contact. These two parts make up jointly the "surface of dissipated energy" (Gibbs).

62. *Equilibrium of two solid phases with liquid phases.*

Two solid phases  $F_1$  and  $F_2$  can be in equilibrium with a liquid phase  $G$ , if a plane laid through the join  $F_1 F_2$  is tangential to the  $\zeta$ -surface at the point  $G$ . For then both  $F_1 G$  and  $F_2 G$  are tangents of the surface. It will readily be seen that the plane  $F_1 F_2 G$  is a common tangential plane of the two tangential cones with  $F_1$  and  $F_2$  as vertices. The surface of dissipated energy consists in this case of the triangle  $F_1 F_2 G$ , the cones with  $F_1$  and  $F_2$  as vertices, outside the triangle and up to the curve of contact on the  $\zeta$ -surface, and finally, of the  $\zeta$ -surface itself outside the curve of contact.

63. *Equilibrium between two liquid phases.*

Let us now investigate the equilibrium between two liquid phases  $H$  and  $K$ . We will first consider the section of the  $\zeta$ -surface by a vertical plane laid through the  $\zeta$ -points  $H$  and  $K$  and prove, as before, that if  $H$  and  $K$  are in equilibrium with each other, the line  $HK$  must be a tangent at  $H$  as well as at  $K$ . Next, let  $h$  and  $k$  (Fig. 20) be the projections of  $H$  and  $K$  upon the fundamental plane,  $l$  and  $L$  points belonging to some complex  $(H, K)$ , so that  $lL$  is its thermodynamical potential, and  $h', k'$  two points collinear with  $l$  and infinitely close to  $h, k$ . Finally, let  $H'$  and  $K'$  be points of the  $\zeta$ -surface of which  $h'$  and  $k'$  are the projections. The complex consisting of  $H$  and  $K$  can then transform itself, by an infinitesimal change of state, into the complex  $H', K'$  to which in the fundamental plane corresponds again the point  $l$ . Since in this process the thermodynamical potential cannot change, the line  $H'K'$  must pass

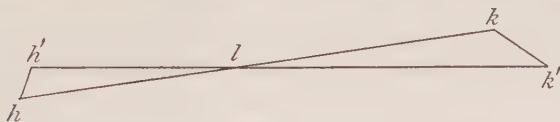


FIG. 20.

through  $L$ . Thus the four points  $H, K, H', K'$  will lie in one plane which, moreover, is tangential to the  $\zeta$ -surface at  $H$  as well as at  $K$ , since  $HK$  is a tangent and  $HH', KK'$  are line-elements of the  $\zeta$ -surface. Consequently, the condition of coexistence of two liquid phases is that the tangential planes laid through the two points in question to the  $\zeta$ -surface shall coincide. In other words, to find two coexistent liquid phases we have only to lay a double tangential plane to the  $\zeta$ -surface.

This, of course, is possible only when the surface has a plait. Having in this case found a pair of coexisting phases, other pairs will be obtained by rolling the double tangential plane over the  $\zeta$ -surface. If the plait extends up to one of the boundary curves of the  $\zeta$ -surface, we then arrive finally at an equilibrium between two phases which contain only two components. If, however, the plait does not extend so far, the two points of contact, for a given position of the tangential plane, coincide with each other or, in physical terms, the two coexisting phases, as regards composition and other properties, continually approach each other

and finally become equal. The point of the  $\zeta$ -surface at which this coincidence takes place is called a *plaitpoint*.

64. Also in the case of three, similarly as in that of two components, the  $\zeta$ -surface can be constructed in a variety of ways by giving special values to the coefficients appearing in the relations between  $m_1$ ,  $m_2$ ,  $m_3$  and  $x$ ,  $y$ . Thus, for example, the solutions can always be taken with a unit weight of water, and with  $x$  and  $y$  units of the second and the third component respectively. The graphical representation of every combination will again be obtained by measuring  $x$  and  $y$  along two perpendicular axes. The surface then extends to infinity along these axes and mounts infinitely high above them.

An example of the application of this method is afforded by Schreinemakers' investigation on the equilibrium of solid  $PbJ_2$ , solid  $KJ$ , their double salt, and solution. The point of the fundamental plane representing solid  $KJ$  lies at infinity on the  $x$ -axis and that representing solid  $PbJ_2$ , at infinity on the  $y$ -axis, while the point for any double salt (of which a quantity containing a unit weight of water is taken) is determined by the corresponding values of  $x$ ,  $y$  as co-ordinates. The enveloping cones for the solid  $PbJ_2$  and  $KJ$  now become enveloping cylinders. The equilibria for every two of the solid phases with a liquid phase can be found by the method explained above. But we shall not enter into the details of this subject.

65. *Mixed crystals*.—We will now give a brief account of the use of the  $\zeta$ -surface in the case of *mixed crystals*.

A solution which at a given pressure and temperature is in equilibrium with two salts has in general a determined composition, independent of the proportion of the solid salts which lie at the bottom. How this solution can be determined by means of the  $\zeta$ -surface was already explained in Art. 62. As was noticed by Rüdorff, however, there are cases in which the composition of the solution is not determined, viz. if the two substances crystallise together. Such is the case of so-called mixed crystals. These were further investigated by Retgers and Bakhuis Rozeboom. It appears that all properties of a mixed crystal are continuous functions of its composition.

This case is more conveniently treated by a graphic representation differing from that of the preceding Article in which the points corresponding to the pure salts were at infinity.



We take a solution or a solid phase which contains of the salts  $A$  and  $B$  together one weight unit, say  $1-x$  of  $A$  and  $x$  of  $B$ , and the quantity  $y$  of water. The composition of a phase is then determined by  $x$  and  $y$ , and in the graphical representation thus set up the values of  $x$  are contained between 0 and 1, and those of  $y$  between 0 and  $\infty$ , while for the two solid phases [pure salts]  $y=0$ ,  $x=1$  and  $y=0$ ,  $x=0$  respectively. The surface is thus bounded by two parallel vertical planes and a third vertical plane perpendicular to these. In the  $x\zeta$ -plane lie the points of the  $\zeta$ -surface which belong to mixtures of the two melted salts, and the parallel vertical planes contain two more curves representing the thermodynamical potential of the solutions of either salt in water. The surface touches the three vertical planes along these lines (cf. footnote on p. 80).

66. Now for the equilibrium between the mixtures and the solutions. A mixed crystal is something else than a simple complex. Its  $\zeta$ -point, therefore, will not lie upon the join of the  $\zeta$ -points belonging to each of the two solid salts but, say, below this straight line, and the  $\zeta$ -points of all mixed crystals (consisting of the two components) will form a curve in the  $x\zeta$ -plane. Now, to find, for a mixed crystal of given composition, the solution with which it can be in equilibrium, we have to lay a plane tangential to this curve and to the  $\zeta$ -surface. If the composition of the mixed crystal is altered, this tangential plane and therefore also the solution with which the crystal is in equilibrium varies, in accordance with Rüdorff's experiments. If we start from one of the components in solid state, this will be in equilibrium with a solution in which also the same component only is contained; if there is a trace of the second component in the mixed crystal, there will be also some of it in the solution but not in the same proportion as in the mixed crystal.

The case that not all compositions of the mixed crystal are possible will be characterised by a  $\zeta$ -curve which is partly concave downwards; the curve has then a double tangent, and the tangential plane to the  $\zeta$ -surface passing through this double tangent marks a solution which can be in equilibrium with two mixed crystals of different composition.

67. Lastly, let us consider the following question: Can the indeterminateness occurring in the thermodynamical potential

through the internal energy and the entropy affect the final results? The thermodynamical potential contains the expression  $C - TC'$ , which for constant temperature is a mere constant. If this constant is given different values, the length of the perpendiculars upon the  $xy$ -plane will be altered, but this change will be such as not to have any influence upon the results concerning equilibria. To see this it is enough to consider, for example, the case of Fig. 14 and to show that one finds always the same composition for the liquid phases which can be in equilibrium with the solid phase  $A$ .

The point at issue is that if two phases or complexes consist of the same quantities of the components, and thus can be transformed into each other, their energies, and similarly their entropies and thermodynamical potentials, must differ by a *determined* amount, although the expressions for these magnitudes for either phase contain undetermined constants.

Now, suppose the figure constructed and the tangents from  $A$  to the  $\zeta$ -line drawn for certain values of the constants. If then by giving the constants other values the thermodynamical potential of the first component taken by itself increases by  $a_1$ , and that of the second component by  $a_2$ , the thermodynamical potential of a complex of  $1-x$  gram molecules of the first and  $x$  gram molecules of the second component will increase by  $(1-x)a_1 + xa_2$ . By what has just been said this will also be the increment of the thermodynamical potential of a homogeneous mixture of a composition determined by  $x$ . The change of the figure consisting of the point  $A$  and the  $\zeta$ -line will thus amount to this, that every point will be displaced upwards over a distance which will be a linear function of  $x$ . The tangents from  $A$  to the curve which share in this deformation will remain straight lines and tangential to the curve. Thus the point of contact will be only displaced upwards, but its abscissa  $x$ , which determines the composition of the mixture, will remain the same.

To prove the last statement about the tangents, it is enough to notice that three collinear points remain collinear after the said deformation, and to take as such three points the point  $A$  and a pair of infinitely close points which the tangent drawn from  $A$  can be considered to have in common with the curve.

68. In treating the  $\zeta$ -surfaces we have limited ourselves, as regards their form, to general considerations. We will now

enter into this matter somewhat further with the aid of van der Waals' theory of mixtures. Instead of the thermodynamical potential, however, we shall now make use of the free energy.

In order to determine the free energy of a mixture we must know its internal energy and entropy. We will first try to deduce the entropy of a mixture of two perfect gases. For this purpose we must first know the entropy of either gas. We will then mix the two gases by a reversible process and thus determine the difference in entropy between the two gases taken separately and the mixture.

Such a reversible mixing can be accomplished by means of external forces. We will choose as the most convenient one the force of gravity and assume, in accordance with the kinetic theory of gases, that either gas spreads over the whole volume as if the other gas were absent. Let us, then, imagine a vertical column of two gases, *e.g.* hydrogen and oxygen, mixed together. Owing to the difference in their density the proportion of the two gases at different heights of the column will be different.

How the density of a gas which alone occupies a space varies from point to point, follows from ordinary aerostatics by noticing that the weight of a volume-element in equilibrium is carried by the difference of pressures from below and from above.

Let  $\rho_1$  and  $p_1$  be the density and the pressure of the first gas at any point of the column and let  $p_1 = c_1 \rho_1$ .

If the positive  $z$ -axis points vertically upwards, the change of pressure  $dp_1$  corresponding to an increment  $dz$  in height is

$$dp_1 = -\rho_1 g dz,$$

whence

$$\frac{d\rho_1}{dz} = -\frac{g}{c_1} \rho_1$$

and

$$\rho_1 = \rho_{1(0)} e^{-\frac{g}{c_1} z}, \quad . \quad . \quad . \quad . \quad (74)$$

where  $\rho_{1(0)}$  is the density for  $z=0$ . Similarly, for the second gas,

$$\rho_2 = \rho_{2(0)} e^{-\frac{g}{c_2} z}.$$

Since  $c_1$  and  $c_2$  are different, the density gradients for the two gases will be different.

69. Let us consider three horizontal layers of the column at the heights  $A$ ,  $B$ , and  $C$ , where  $A$  corresponds to the middle and  $B$  to the highest layer. Now, it is always possible to mix together quantities of gas having the composition of  $B$  and of  $C$  so as to

obtain a quantity of the composition of  $A$ , and *vice versa*, a quantity of the composition of  $A$  can be split into two quantities having the composition of  $B$  and of  $C$ .

This mixing and separating can be accomplished as reversible processes by applying at  $A$ ,  $B$ ,  $C$  horizontal pipes which protrude from the column and are fitted out with pistons. Thus some gas can be removed from the column at  $B$  and  $C$  by moving the pistons, say, towards the right, while at  $A$  a quantity of gas mixture there present can be pressed into the column by moving the piston towards the left. We assume that each tube contains also some gas mixture of the same composition as the layer of the column to which it is applied.

Now, let  $AB = AC = l$ , and let  $\rho_1, p_1, \rho_2, p_2$  correspond to  $A$ ;  $\rho'_1, p'_1, \rho'_2, p'_2$  to  $B$ , and  $\rho''_1, p''_1, \rho''_2, p''_2$  to  $C$ . Further, put

$$\rho'_1 = \frac{\rho_1}{k_1}, \quad \rho'_2 = \frac{\rho_2}{k_2}.$$

Then  $\rho''_1 = k_1 \rho_1, p'_1 = \frac{p_1}{k_1}, p''_1 = k_1 p_1$

and  $\rho''_2 = k_2 \rho_2, p'_2 = \frac{p_2}{k_2}, p''_2 = k_2 p_2.$

Let a unit volume at  $A$  contain the same amounts of both gases as a volume  $x'$  at  $B$  and a volume  $x''$  at  $C$  taken together. Then the values of  $x'$  and  $x''$  will be determined by the equations

$$\rho'_1 x' + \rho''_1 x'' = \rho_1$$

and  $\rho'_2 x' + \rho''_2 x'' = \rho_2.$

These give

$$x' = \frac{k_1 k_2}{k_1 + k_2}, \quad x'' = \frac{1}{k_1 + k_2}.$$

We will now split the mixture by a reversible process and compute the required work.

Thus, let us introduce a unit volume of mixture into the column at  $A$  and take out  $x'$  and  $x''$  units at  $B$  and  $C$  respectively.

The total work done in this process is

$$p_1 + p_2 - (p'_1 + p'_2)x' - (p''_1 + p''_2)x'',$$

which after the substitutions of the values for  $x'$  and  $x''$  turns out to be nil.

There is here a subtlety in play : The two mixtures  $B$  and  $C$  into which  $A$  has been split are brought to a different level and have thus acquired a different potential energy. And as no work has been done, this is only possible if the system which is kept at a constant temperature has received or given up heat. From the change of potential energy the quantity of heat supplied and thence also the change of entropy will now be determined.

The increase of potential energy is obviously

$$\{x'(\rho'_1 + \rho'_2) - x''(\rho''_1 + \rho''_2)\}gl,$$

and this is equal to the heat supplied, so that the increase in entropy is

$$\frac{1}{T}\{x'(\rho'_1 + \rho'_2) - x''(\rho''_1 + \rho''_2)\}gl = -\frac{1}{T} \frac{k_1 - k_2}{k_1 + k_2}(\rho_1 - \rho_2)gl. \quad (75)$$

This is the excess of the entropy of a volume  $x'$  of the mixture  $B$  and a volume  $x''$  of the mixture  $C$  over the entropy of a unit volume of  $A$ . We will now derive from it those volumes  $y'$  and  $y''$  of  $B$  and  $C$  whose total entropy is equal to that of a unit volume of  $A$ . For this purpose the sum of the change of entropy of the mixture  $B$  due to a reversible isothermal change of its volume from  $x'$  to  $y'$  and of the corresponding change of entropy of  $C$  in passing from  $x''$  to  $y''$  has to be equated to the expression (75) with inverted sign. Now, the former change of entropy is readily found to be

$$\frac{1}{T}x'(\rho'_1 + \rho'_2) \log \frac{y'}{x'},$$

and the latter,

$$\frac{1}{T}x''(\rho''_1 + \rho''_2) \log \frac{y''}{x''},$$

so that

$$x'(\rho'_1 + \rho'_2) \log \frac{y'}{x'} + x''(\rho''_1 + \rho''_2) \log \frac{y''}{x''} = \frac{k_1 - k_2}{k_1 + k_2}(\rho_1 - \rho_2)gl. \quad (76)$$

Substituting

$$\rho'_1 + \rho'_2 = \frac{p_1}{k_1} + \frac{p_2}{k_2} = \frac{c_1 \rho_1}{k_1} + \frac{c_2 \rho_2}{k_2}$$

and

$$\rho''_1 + \rho''_2 = c_1 k_1 \rho_1 + c_2 k_2 \rho_2,$$

each term of (76) will be found to contain either  $\rho_1$  or  $\rho_2$  as a factor. This equation will therefore be satisfied if the terms



with  $\rho_1$  and those with  $\rho_2$  balance separately. Thus, after the substitution of the values of  $x'$  and  $x''$  found above,

$$c_1 \left\{ k_2 \log \frac{y'}{x'} + k_1 \log \frac{y''}{x''} \right\} = (k_1 - k_2)gl,$$

$$c_2 \left\{ k_1 \log \frac{y'}{x'} + k_2 \log \frac{y''}{x''} \right\} = -(k_1 - k_2)gl,$$

whence

$$\log \frac{y'}{x'} = -gl \frac{k_1 c_1 + k_2 c_2}{(k_1 + k_2)c_1 c_2}, \quad . \quad . \quad . \quad (77)$$

$$\log \frac{y''}{x''} = gl \frac{k_1 c_2 + k_2 c_1}{(k_1 + k_2)c_1 c_2} \quad . \quad . \quad . \quad (78)$$

Equation (76) can, of course, be satisfied also by other values of  $y'$  and  $y''$ , but it is enough for us to know that the sum of the entropies of the volumes  $y'$  and  $y''$  of the mixtures  $B$  and  $C$  given by (77) and (78) is equal to the entropy of the mixture  $A$  from which they were obtained.

70. Let now the distance  $l$  become very great, the point  $A$  being kept fixed and  $B$  and  $C$  moving farther and farther away from it. By letting  $l$  tend to infinity we can approach the complete separation of the gases as nearly as we please. In fact, the mixture  $B$  contains the quantity

$$\rho'_1 x' = \frac{k_2 \rho_1}{k_1 + k_2}$$

of the first, and the quantity

$$\rho'_2 x' = \frac{k_1 \rho_2}{k_1 + k_2}$$

of the second gas, while the mixture  $C$  contains the quantities

$$\frac{k_1 \rho_1}{k_1 + k_2} \quad \text{and} \quad \frac{k_2 \rho_2}{k_1 + k_2}$$

of the first and the second gas respectively. Thus the weight ratio of the two gases is  $k_2/k_1$  for the mixture  $B$  and  $k_1/k_2$  for  $C$ . Now,

$$k_1 = e_{c_1}^g l, \quad k_2 = e_{c_2}^g l, \\ \frac{k_2}{k_1} = e^{gl \left( \frac{1}{c_2} - \frac{1}{c_1} \right)}, \quad \frac{k_1}{k_2} = e^{gl \left( \frac{1}{c_1} - \frac{1}{c_2} \right)}.$$

If, therefore,  $c_1 > c_2$ , we have  $k_1 < k_2$  and, for  $l \rightarrow \infty$ ,  $k_2/k_1$  tends to infinity and  $k_1/k_2$  to zero. Thus, passing to the limit, we

may say that at  $B$  only the first and at  $C$  only the second gas has been removed from the column. This seems somewhat strange. If we consider a mixture of hydrogen and oxygen, then it is true that high up in the column the density of hydrogen is much less reduced than that of oxygen, and we can even imagine that at a very high level there is almost pure hydrogen. But the density of hydrogen is also very great at the bottom of the column. We must remember, however, that oxygen is there condensed, in a yet much higher degree, so that in comparison the quantity of the hydrogen amounts to nothing.

Returning to the volumes  $y'$  and  $y''$ , which had to be given to  $B$  and  $C$  in order to make the sum of their entropies equal to the entropy of a unit volume of  $A$ , let us see what they become for  $l = \infty$ . Since  $k_1/k_2$  tends to zero, we have at the limit, by (77),

$$\log \frac{y'}{x'} = -\frac{gl}{c_1},$$

whence

$$\frac{y'}{x'} = e^{-\frac{gl}{c_1}} = \frac{1}{k_1}, \quad y' = \frac{x'}{k_1} = \frac{k_2}{k_1 + k_2},$$

and therefore,  $\lim y' = 1$ . Similarly  $\lim y'' = 1$ . We thus arrive at the conclusion that *the entropy of a mixture of two gases is equal to the sum of their entropies, provided that either gas taken separately occupies at the same temperature the same volume as the mixture.*

This is known as Gibbs' paradox. What there is paradoxical about it will appear presently.

Gibbs' paradox can also be proved by imagining a membrane which is permeable for one gas but not for the other. By moving it across the mixture the latter component can be swept away. This method does not in essence differ very much from the preceding one. In both methods the possibility is assumed of influencing the density of the two gases by means of external forces in different degrees.

71. The theorem can also be extended to mixtures of three or more gases. This will be seen most readily by introducing for each gas an appropriate external force which would tend to concentrate the gas around a certain point, the concentration points for the several gases being chosen at different places.

What was proved for the entropy will hold as well for the

free energy, if it be assumed that the mixing of the gases is taking place at constant temperature and volume and without generation or absorption of heat, so that the energy  $\epsilon$  of the mixture is equal to the sum of the energies of the components.

Now, an expression for the free energy of a mixture of any number of gases can readily be found. Let  $n$  be the number of components,  $v$  the volume of the mixture consisting of  $m_1, m_2, \dots m_n$  units of these components, and  $R_1, R_2, \dots R_n$  their gas constants, per unit. Then the total free energy of the mixture will be, by (50) in conjunction with Gibbs' theorem,

$$\Psi = -m_1 R_1 T \log \frac{v}{m_1} - m_2 R_2 T \log \frac{v}{m_2} - \dots$$

$$\text{or} \quad \Psi = -T \log v \cdot \Sigma(mR) + T \Sigma(mR \log m), \quad (79)$$

where the summations are to be extended over all components.

72. The diminution of the free energy of two gases which takes place when the gases mix with each other at constant temperature and preserving their joint volume can now also be calculated. This is, by Gibbs' theorem, equal to the diminution for both gases taking place when either gas is brought, at constant temperature, to their joint volume. Let us take, for instance, a gram molecule of each gas. Then, if both gases were originally under the same pressure and each had, therefore, the same volume  $v$ , the volume of the mixture will be  $2v$ . Thus, each gas expands from  $v$  to  $2v$  and, according to (49), its free energy diminishes by  $RT \log 2$ . Consequently the required total diminution will be

$$2RT \log 2.$$

It will be well to emphasise that this value is independent of the nature of the gases and will remain the same, no matter how little they differ from each other in molecular weight. Yet it would be wrong to apply this result to the mixing of two portions of the same gas. In fact, if two such perfectly equal gas quantities are originally separated by a wall, then, if this is removed, the free energy does not change at all. In fine, the case of two equal gases can *not* be considered as the limiting case of a system of two different gases. That this sounds somewhat paradoxically, cannot be denied. Whence also the name given to Gibbs' theorem. The puzzling effect of the conclusion is hard to remove. We can only say that the proof of

Gibbs' theorem given above continues to hold so long as the two gases differ from each other, no matter how slightly, but ceases to hold if they are perfectly equal, and that in its applications the theorem has not led to discrepancies.

73. We will now endeavour to determine the free energy of a mixture which occurs in the liquid state or, at any rate, is no perfect gas. This can be accomplished by imagining the mixture converted by an isothermal expansion into a perfect gas. It will be assumed that during this process the mixture remains permanently homogeneous.

Further, the law of van der Waals, as given in Part II. of his *Continuität des gasförmigen und flüssigen Zustandes*, will be assumed to hold for mixtures.

For a binary mixture, of  $1-x$  gram molecules of the first and  $x$  gram molecules of the second substance, this law can be written

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT, \quad . \quad . \quad . \quad (80)$$

where the constants  $a$ ,  $b$  expressing the effect of the molecular attraction and the finite dimensions of the particles are given by

$$\begin{aligned} a &= (1-x)^2 a_1 + 2x(1-x) a_{12} + x^2 a_2, \\ b &= (1-x)^2 b_1 + 2x(1-x) b_{12} + x^2 b_2. \end{aligned}$$

Here  $a_1$  is the constant of molecular attraction for the first,  $a_2$  that for the second substance, and  $a_{12}$  the constant of mutual attraction of the two substances, while  $b_1$  and  $b_2$  are identical with van der Waals'  $b$  for the first and the second substance, *i.e.* four times the molecular volume of a gram molecule. Finally,  $b_{12}$  is derived from  $b_1$  or  $b_2$  by replacing therein the diameter of a molecule by half the sum of the diameters of the two kinds of molecules.

Instead of  $b$  the more simple expression

$$b' = b_1(1-x) + b_2 x$$

is used, and in view of all the difficulties of the theory not much can be said against this substitution, although the first expression for  $b$  is more correct.

We will assume that at a fixed temperature  $T$  the free energy of a gram molecule of either gas when occupying a certain volume  $w$  is nil. This will fix the values of our unknown

constants. The volume  $w$  will be assumed large enough to enable us to consider either substance, when occupying it, as a perfect gas. Further, let  $V$  be some very large volume and  $v$  the actual volume of our mixture. Then the free energy of the mixture can be written

$$\Psi_v = \Psi_V - \int_v^V \frac{\partial \Psi}{\partial v} dv = \Psi_V + \int_v^V p dv,$$

since, by (45),  $\partial \Psi / \partial v = -p$ . Thus, by (80),

$$\Psi_v = \Psi_V + \int_v^V \left\{ \frac{RT}{v-b} - \frac{a}{v^2} \right\} dv = \Psi_V + a \left( \frac{1}{V} - \frac{1}{v} \right) + RT \log \frac{V-b}{v-b}.$$

Now, by Gibbs' theorem,  $\Psi_V$  is equal to the sum of the free energies which either component would possess if it occupied by itself the volume  $V$ .

The free energy of  $1-x$  gram molecules of the first gas occupying the volume  $V$  is, by (49) and remembering how the undetermined constant was fixed,

$$(1-x)RT \log \frac{(1-x)w}{V}.$$

Similarly, for the  $x$  gram molecules of the second gas,

$$xRT \log \frac{xw}{V}.$$

Thus,

$$\Psi_v = RT \left\{ (1-x) \log \frac{(1-x)w}{V} + x \log \frac{xw}{V} \right\} + a \left( \frac{1}{V} - \frac{1}{v} \right) + RT \log \frac{V-b}{v-b}.$$

The greater the volume  $V$ , the more accurate the result. Let us therefore make  $V$  tend to infinity. Then

$$\begin{aligned} \Psi_v = -\frac{a}{v} - RT \log (v-b) + RT \log \frac{V-b}{V} \\ + RT \{ (1-x) \log (1-x) + x \log x \} + RT \log w. \end{aligned}$$

The third term vanishes, and the last term is for a fixed temperature a constant which can be omitted. Thus, ultimately,

$$\Psi_v = -\frac{a}{v} - RT \log (v-b) + RT \{ (1-x) \log (1-x) + x \log x \}. \quad (81)$$

This is the formula used always by van der Waals.

The last term represents the phenomena when one of the components is present in a very small amount (properties of



diluted solutions, osmotic pressure, vapour pressure, etc.), in which case the numerical agreement of the theory with the experimental facts is excellent. The first two terms are unsatisfactory inasmuch as they depend on the equation of state [such as (80)], which is not known well enough, and thus carry into the expression of  $\Psi$  all the faults of that equation.

74. In connection with the last remark the question arises whether the third term would still appear in  $\Psi_v$  if we knew the correct characteristic equation. In order to answer this question we will once more deduce the value of  $\Psi_v$  without making any particular assumption about the form of the characteristic equation.

We write again

$$\Psi_v = \Psi_V + \int_v^V p dv$$

and put

$$p = \frac{RT}{v} + p',$$

so that  $p'$  is the excess of the actual pressure over that which would correspond to a gram molecule of a perfect gas. Then

$$\Psi_v = \Psi_V + RT \log \frac{V}{v} + \int_v^V p' dv$$

or, substituting the value of  $\Psi_V$  found above,

$$\Psi_v = RT(1-x) \log \frac{(1-x)w}{V} + RTx \log \frac{xw}{V} + RT \log \frac{V}{v} + \int_v^V p' dv.$$

Thus, if  $V$  is again made to increase indefinitely and the constant term  $RT \log w$  is omitted,

$$\Psi_v = \int_v^\infty p' dv - RT \log v + RT \{(1-x) \log (1-x) + x \log x\}. \quad (82)$$

If the volume becomes very large,  $p'$  becomes very small, since the substance behaves then almost as a perfect gas, and we can imagine that for large values of  $v$  the integral  $\int_v^\infty p' dv$  remains finite and even becomes small.

We see that the last term in (82) is exactly the same as in the value of  $\Psi_v$  found before.

Similarly  $\Psi_r$  can be found for three or more components.

If the mixture contains  $x$ ,  $y$ , and  $1 - x - y$  gram molecules of the three components, the last term becomes

$$RT\{x \log x + y \log y + (1 - x - y) \log (1 - x - y)\}.$$

If, as is most often done by chemists, one prefers to use the thermodynamical potential instead of the free energy, the same last term will reappear.

75. We shall see later on what important rôle the last term of (81) or (82) plays when one of the components is present in a very small amount. Meanwhile we will mention only that for  $x=0$  and  $x=1$  the free energy  $\Psi_v$  remains finite (for, when  $x$  tends to 0, this is also the case of  $x \log x$ ), but that for these extreme values of  $x$  the derivative  $\partial \Psi_v / \partial x$  becomes infinite. In fact, by (81),

$$\frac{\partial \Psi_v}{\partial x} = -\frac{1}{v} \frac{da}{dx} + \frac{RT}{v-b} \frac{db}{dx} + RT \log \frac{x}{1-x},$$

and here the last term becomes  $-\infty$  for  $x=0$  and  $+\infty$  for  $x=1$ .

The same results hold good for the thermodynamical potential of a mixture, since this also contains a term identical with the last one of (81). We thus see that in our figures (as *e.g.* Fig. 14) representing the  $\zeta$ -line for a mixture the extremities of this line ( $x=0$  and  $x=1$ ) were with good reason placed at a finite height and the  $\zeta$ -line at these points drawn vertically.

76. *Equilibrium of two phases consisting of two components.*

We will next apply the above theory to some special cases. Let us consider two phases in contact with one another, each phase consisting of the same two components but in different proportions. In order to find the equilibrium of this system we shall avail ourselves of the free energy which in a state of equilibrium must be a minimum, the total volume and the temperature being kept constant.

As before, let a gram molecule of a phase, which will be our unit, contain  $1-x$  gram molecules of the first, and  $x$  gram molecules of the second component. The state of a gram molecule of the phase will be completely determined by its volume  $v$  and by the value of  $x$  which fixes its composition. We will write, in particular,  $x$  and  $v$  for the first, and  $x'$  and  $v'$  for the second phase. The amounts of the two phases expressed in gram molecules will be denoted by  $n$  and  $n'$  respectively.

If  $N$  be the number of molecules contained in a gram molecule, the total number of molecules of the second component will be  $N(nx + n'x')$  and that of all molecules of both components  $N(n + n')$ .

Further, let  $\Psi$  be the free energy of a unit of the first, and  $\Psi'$  that of a unit of the second phase. Then the total free energy of the system will be

$$n\Psi + n'\Psi'.$$

In order to find its minimum the system has to be subjected to an infinitesimal change. The possible changes are :

1°. A displacement of the separating surface of the two phases accompanied by the increase of the volume of one phase at the expense of the other.

2°. The passage of a small quantity of one component from one to the other phase, while the interface remains fixed.

The condition of equilibrium is that the increase of the free energy in each of these changes and their combinations shall be zero. Thus,

$$\Psi\delta n + n\delta\Psi + \Psi'\delta n' + n'\delta\Psi' = 0,$$

*i.e.*

$$\Psi\delta n + n\left(\frac{\partial\Psi}{\partial x}\delta x + \frac{\partial\Psi}{\partial v}\delta v\right) + \Psi'\delta n' + n'\left(\frac{\partial\Psi'}{\partial x'}\delta x' + \frac{\partial\Psi'}{\partial v'}\delta v'\right) = 0. \quad (83)$$

The several variations are not independent of each other, so that we cannot simply equate to zero all the coefficients. The supplementary condition is that the total amount of either component shall be constant, or also, that the quantity of one component and the sum of the quantities of both components shall remain constant, *i.e.*

$$N(n + n') = \text{const.}, \text{ and } N(nx + n'x') = \text{const.}$$

$$\text{or} \quad \delta n + \delta n' = 0, \quad x\delta n + x'\delta n' + n\delta x + n'\delta x' = 0.$$

Again, the total volume,  $nv + n'v'$ , must remain constant, *i.e.*

$$v\delta n + v'\delta n' + n\delta v + n'\delta v' = 0.$$

Equation (83) has now to be satisfied by variations subject to these three conditions. Three variations, say  $\delta x'$ ,  $\delta v'$ ,  $\delta n'$ , can thus be eliminated and the coefficients of the remaining three

in the resulting equation have to be equated to zero. This gives, after some simple reductions,

$$\frac{\partial \Psi}{\partial x} = \frac{\partial \Psi'}{\partial x'}, \quad . \quad . \quad . \quad . \quad . \quad (84)$$

$$\frac{\partial \Psi}{\partial v} = \frac{\partial \Psi'}{\partial v'} \quad \text{or} \quad p = p', \quad . \quad . \quad . \quad . \quad . \quad (85)$$

and 
$$\Psi - x \frac{\partial \Psi}{\partial x} - v \frac{\partial \Psi}{\partial v} = \Psi' - x' \frac{\partial \Psi'}{\partial x'} - v' \frac{\partial \Psi'}{\partial v'}. \quad . \quad . \quad . \quad . \quad . \quad (86)$$

These are three relations between the four variables  $x$ ,  $v$ ,  $x'$ ,  $v'$ . One of the latter can therefore be chosen arbitrarily, as was to be expected.

A better insight into all these relations can be obtained by means of van der Waals'  $\Psi$ -surface which will be taken up in the sequel.

#### 77. *A mixture under the influence of external forces.*

Let us now consider a mixture [of two components in one phase, as in Art. 74] acted upon by external forces. We shall limit ourselves to the force of gravity. The state at any height will again be determined by  $x$  and  $v$ , representing the composition and the volume of a gram molecule and thus also the density at any point of the mixture. The positive  $z$ -axis will be drawn vertically upwards. At each point of a plane perpendicular to the  $z$ -axis the state will be the same. The total volume is constant. Under this condition the substance will distribute itself so as to make the free energy of the system a minimum. The free energy will be given by the sum of the expression (82) and the potential energy due to gravity.

Consider a vertical column of unit cross-section. A volume-element of height  $dz$  [at a level  $z$ ] contains  $dz/v$  gram molecules of mixture, *i.e.*

$$(1-x) \frac{dz}{v} \text{ gram molecules or } M_1(1-x) \frac{dz}{v} \text{ grams}$$

of the first, and

$$x \frac{dz}{v} \text{ gram molecules or } M_2 x \frac{dz}{v} \text{ grams}$$

of the second component. Thus its potential energy due to gravity is

$$\left\{ M_1(1-x) \frac{dz}{v} + M_2 x \frac{dz}{v} \right\} gz,$$

and the expression which for the state of equilibrium must be a minimum,

$$\Psi' = \int \frac{\Psi'}{v} dz + M_1 \int (1-x)gz \frac{dz}{v} + M_2 \int xgz \frac{dz}{v}, \quad (87)$$

where  $\Psi$  has the value (82).

The quantities  $x$  and  $v$  are functions of  $z$ . Their variations are subject to the conditions following from the invariability of the total amount of each component. These conditions are :

$$\delta \int M_1(1-x) \frac{dz}{v} = 0, \text{ which will be written } \delta\chi = 0, \quad (88)$$

and

$$\delta \int M_2 x \frac{dz}{v} = 0, \text{ which will be written } \delta\Phi = 0. \quad (89)$$

78. The process of elimination can be accomplished as in previous cases. We multiply (88) and (89) by constant factors  $\mu_1$  and  $\mu_2$  and add to the developed equation

$$\delta\Psi' = 0, \quad (90)$$

where  $\Psi'$  is as in (87). The result is that the derivatives of  $\Psi' + \mu_1\chi + \mu_2\Phi$ , i.e., of the integral

$$\int [\Psi + M_1(1-x)(gz + \mu_1) + M_2x(gz + \mu_2)] \frac{dz}{v} \quad (91)$$

with respect to  $x$  and to  $v$  must vanish for every  $z$ .

This differentiation amounts to varying  $x$  or  $v$  at a given place and keeping their values unaltered elsewhere. The integration sign can thus be omitted and the conditions of equilibrium become

$$\frac{1}{v} \frac{\partial \Psi}{\partial v} - \frac{1}{v^2} \{\Psi + M_1(1-x)(gz + \mu_1) + M_2(gz + \mu_2)\} = 0 \quad (92)$$

$$\text{and} \quad \frac{\partial \Psi}{\partial x} - M_1(gz + \mu_1) + M_2x(gz + \mu_2) = 0, \quad (93)$$

where  $\mu_1$  and  $\mu_2$  are constants.

The equations (92) and (93) can be imagined to be solved for  $\mu_1$  and  $\mu_2$ , so that ultimately the equilibrium conditions assume the form of two functions of  $x, v, z$  equated to constants, say,

$$F_1(x, v, z) = \mu_1 \quad \text{and} \quad F_2(x, v, z) = \mu_2.$$



If  $x$  and  $v$  are given for a certain height  $z$  within the column, the values of  $\mu_1$  and  $\mu_2$  can be determined. If  $x$  is very small, the term with  $\log x$  in the expression for the derivative  $\partial\Psi/\partial x$  (cf. Art. 75) becomes by far the most relevant, and  $\partial\Psi/\partial x$  reduces to  $RT \log x$ .

Equation (93) can then be written

$$RT \log x = (M_1 - M_2)gz + M_1\mu_1 - M_2\mu_2$$

or

$$RT \log x = (M_1 - M_2)gz + C.$$

This gives

$$x = x_0 e^{\frac{M_1 - M_2}{RT}gz}, \quad . \quad . \quad . \quad (94)$$

where  $x_0 = e^{C/RT}$ . According to the sign of  $M_1 - M_2$  the value of  $x$  will increase or decrease with increasing height.

Thus, in a diluted solution in water (first component) of a salt of greater molecular weight the concentration will decrease upwards, since  $M_1 - M_2$  is negative, and it will increase upwards for a lighter salt. For  $M_1 = M_2$  the concentration will be everywhere the same.

79. We will now take another case of a mixture acted upon by an external force. This case will approach that of osmotic pressure.

Let us consider a solution acted upon by a conservative external force which drives the solute in a certain direction. Owing to this force both substances, the solvent and the solute, will possess some potential energy. Let this be  $\mathbf{P}_1$  per gram molecule of the former and  $\mathbf{P}_2$  for the latter substance. We assume for the sake of simplicity that  $\mathbf{P}_1$  and  $\mathbf{P}_2$  depend only on one co-ordinate  $z$ , and consider a column of the solution whose axis coincides with the  $z$ -axis and whose cross-section is 1 cm.<sup>2</sup>. This case has much in common with the preceding one.

We fix our attention upon a layer of thickness  $dz$ . The meaning of the symbols  $x$  and  $v$  being as above, the layer will contain  $(1-x)\frac{dz}{v}$  gram molecules of the first and  $x\frac{dz}{v}$  gram molecules of the second substance. If  $\Psi$  be the free energy per gram molecule of the mixture, apart from the potential energy, the condition of equilibrium will be

$$\delta \int \frac{\Psi + (1-x)\mathbf{P}_1 + x\mathbf{P}_2}{v} dz = 0, \quad . \quad . \quad . \quad (95)$$

since the total free energy of the system must be a minimum. We have again the two supplementary conditions

$$\delta \int \frac{1-x}{v} dz = 0 \quad . \quad . \quad . \quad (96)$$

and 
$$\delta \int \frac{x}{v} dz = 0. \quad . \quad . \quad . \quad (97)$$

The procedure is as before. We multiply (96) and (97) by  $\mu_1$  and  $\mu_2$  and add to (95). Equating to zero the coefficients of all variations in the resulting equation, we find the equilibrium conditions

$$\frac{\partial}{\partial x} \frac{\Psi + (1-x)(\mathbf{P}_1 + \mu_1) + x(\mathbf{P}_2 + \mu_2)}{v} = 0 \quad . \quad . \quad (98)$$

and 
$$\frac{\partial}{\partial v} \frac{\Psi + (1-x)(\mathbf{P}_1 + \mu_1) + x(\mathbf{P}_2 + \mu_2)}{v} = 0. \quad . \quad . \quad (99)$$

These two equations settle the question completely;  $\mu_1$  and  $\mu_2$  are again constants which, by solving (98) and (99), will be found as functions of  $x$ ,  $v$ , and  $z$ . We thus obtain two functions of  $x, v, z$  which are constant. The values of the constants will be found from the data of the problem. From (98) follows

$$\frac{\partial \Psi}{\partial x} - (\mathbf{P}_1 + \mu_1) + (\mathbf{P}_2 + \mu_2) = 0, \quad . \quad . \quad (100)$$

and from (99),

$$\Psi - v \frac{\partial \Psi}{\partial v} + (1-x)(\mathbf{P}_1 + \mu_1) + x(\mathbf{P}_2 + \mu_2) = 0. \quad . \quad (101)$$

Applying the equation (101) to two points at a distance  $dz$  from each other we find

$$\frac{\partial \Psi}{\partial x} dx + v dp - dx(\mathbf{P}_1 + \mu_1) + (1-x)d\mathbf{P}_1 + dx(\mathbf{P}_2 + \mu_2) + x d\mathbf{P}_2 = 0,$$

where  $\partial \Psi / \partial v$  has been replaced by  $-\mu$ . By (100) three terms cancel and we are left with

$$v dp + (1-x)d\mathbf{P}_1 + x d\mathbf{P}_2 = 0, \\ i.e. \quad dp + \frac{1-x}{v} \frac{d\mathbf{P}_1}{dz} dz + \frac{x}{v} \frac{d\mathbf{P}_2}{dz} dz = 0. \quad . \quad . \quad (102)$$

This equation says simply that the increase in pressure in passing from  $z$  to  $z + dz$  is equal to the external force acting upon the included layer, as was to be expected.

If the solution is very diluted,  $\partial\psi/\partial x$  can be approximately replaced by  $RT \log x$  (cf. p. 100), and equation (100) reduces to

$$RT \log x - (\mathbf{P}_1 + \mu_1) + (\mathbf{P}_2 + \mu_2) = 0 \quad (103)$$

or 
$$x = Ce^{\frac{\mathbf{P}_1 - \mathbf{P}_2}{RT}},$$

where  $C = e^{\frac{\mu_1 - \mu_2}{RT}}.$

From this formula we see that the distribution of the dissolved substance over the column is determined not only by the forces acting upon this substance but also by those acting upon the solvent. If there is no force upon the solvent, the concentration is of course greatest where the potential energy of the dissolved substance is smallest. If, on the other hand, the force acts only upon the solvent, the concentration of the solute is smallest where the potential energy of the solvent is smallest.

80. Let us imagine a vessel containing an aqueous solution at the bottom and pure water on the top, separated from one another by a semi-permeable membrane which allows only the solvent to pass. In this manner the solute will always remain in the lower part of the vessel. Now, the same result can be obtained by applying to the solute appropriate forces. Suppose these forces to act within a thin horizontal layer. The greater the forces, the smaller the ratio of concentrations above and below the layer, and in the limit the state of affairs can be imagined to be the same as with a semi-permeable membrane. Since the external forces act only upon the solute, we have  $\mathbf{P}_1 = 0$ , so that equation (103) becomes

$$RT \log x = -\mathbf{P}_2 + \mu_1 - \mu_2,$$

whence

$$d\mathbf{P}_2 = -\frac{RT}{x} dx.$$

Equation (102) reduces to

$$vdp + x d\mathbf{P}_2 = 0,$$

so that

$$vdp = -x d\mathbf{P}_2 = RT dx,$$

i.e.

$$dp = \frac{RT}{v} dx.$$

This expresses the relation between the changes of pressure and of concentration;  $v$  is not a constant, but if the solution is very diluted, the changes of  $v$  can be neglected. In that case we have by integration

$$p_1 - p_2 = \frac{RT}{v} x, \quad (104)$$

where  $x$  is the concentration below the thin layer [of impressed forces]. This is *van 't Hoff's law of osmotic pressure*,  $\frac{RT}{v}x$  being

the pressure which would be exerted by the solute if it were in the gaseous form and occupied the same space as the solution.

81. This deduction is, no doubt, somewhat artificial. Let us therefore reconsider the case, treating it so as it occurs actually, *i.e.* with the semi-permeable membrane. It is true that we do not know the mechanism of such a membrane, but for a thermodynamical reasoning such a knowledge is not needed.

Let us, then, consider the equilibrium of two phases separated by a semi-permeable membrane.

The first phase consists of the pure solvent  $W$ , and the second is a solution in  $W$  of a certain quantity of the substance  $C$ . The solvent is a simple substance in which no components are to be distinguished. The membrane allows only  $W$  to pass, not  $C$ . It will be assumed, moreover, that the walls of the vessel as well as the membrane are fixed, so that no work can be done and the condition of equilibrium is that the total free energy shall be a minimum.

Now, the only change possible is the passage of some solvent across the membrane from one to the other phase.

Let the first phase contain  $n'$  gram molecules of  $W$  and the second  $n(1-x)$  gram molecules of  $W$  and  $nx$  of  $C$ . Let  $v'$  and  $\Psi'$  be the volume and the free energy of a gram molecule of the first phase, and let  $v$  and  $\Psi$  have corresponding meanings for the second phase.

Then, what is to be a minimum is

$$n\Psi + n'\Psi',$$

while the volume of either phase, the total quantity of both substances and that of  $C$ , *i.e.*  $nv$ ,  $n'v'$ ,  $n+n'$ , and  $nx$  are to be kept constant. Thus,

$$n\delta v + v\delta n = 0, \quad n'\delta v' + v'\delta n' = 0,$$

$$\delta n + \delta n' = 0, \quad n\delta x + x\delta n = 0,$$

whence

$$\delta v = -\frac{v}{n}\delta n, \quad \delta v' = -\frac{v'}{n'}\delta n, \quad \delta n' = -\delta n, \quad \delta x = -\frac{x}{n}\delta n. \quad (105)$$

The condition of equilibrium is

$$n\delta\Psi + \Psi'\delta n + n'\delta\Psi' + \Psi'\delta n' = 0,$$

$$\text{i.e.} \quad n\left(\frac{\partial\Psi}{\partial v}\delta v + \frac{\partial\Psi}{\partial x}\delta x\right) + \Psi'\delta n + n'\frac{\partial\Psi'}{\partial v'}\delta v' + \Psi'\delta n' = 0,$$

and after the substitution of (105),

$$\Psi - x\frac{\partial\Psi}{\partial x} - v\frac{\partial\Psi}{\partial v} = \Psi' - v'\frac{\partial\Psi'}{\partial v'}.$$

Now, by (82), we have for the solution

$$\Psi = \int_v^\infty p'dv - RT \log v + RT\{x \log x + (1-x) \log (1-x)\}.$$

The variable  $x$  occurs not only in the last but in the first term also. We shall assume, however, that  $x$  is small and that  $\int_v^\infty p'dv$  can be developed into ascending powers of  $x$  (i.e. that  $p'$  and its derivatives with respect to  $x$  are finite for  $x=0$ ). Then, neglecting the second and higher powers of  $x$ , we can write

$$\int_v^\infty p'dv = \omega + kx.$$

This gives

$$\Psi - x\frac{\partial\Psi}{\partial x} = \omega - RT \log v + RT \log (1-x)$$

$$\text{or} \quad \Psi - x\frac{\partial\Psi}{\partial x} = \Psi_0 + RT \log (1-x),$$

where  $\Psi_0$  is the value of  $\Psi$  for  $x=0$  (and for the volume  $v$ ). The equilibrium condition thus becomes

$$\Psi_0 + RT \log (1-x) - v\frac{\partial\Psi}{\partial v} = \Psi' - v'\frac{\partial\Psi'}{\partial v'}.$$

Here  $\Psi_0$  is the free energy of a gram molecule of the solvent at the volume  $v$  and  $\Psi'$  its free energy at the volume  $v'$ . But since  $v$  and  $v'$  differ but little from each other,  $x$  being assumed small, we can write

$$\Psi_0 - \Psi'' + (v-v')\frac{\partial\Psi'}{\partial v'},$$

so that the equation of equilibrium assumes the form

$$v\left(\frac{\partial\Psi'}{\partial v'} - \frac{\partial\Psi}{\partial v}\right) + RT \log (1-x) = 0$$



or, by (45) and since  $x$  is small,

$$p - p' = RT \frac{x}{v}, \quad . \quad . \quad . \quad . \quad (106)$$

which is again the law of osmotic pressure. This result is independent of the particular form of  $\int p' dv$ .

## 82. General conditions of equilibrium between different phases.

We will now investigate the equilibrium of a system consisting of  $n$  components and  $k$  phases in contact with each other. A *phase* is each homogeneous substance consisting of the  $n$  components or of some of them, and by *components* we mean  $n$  independent substances chosen so that all the phases can be composed of them. The choice, moreover, is to be such that  $n$  is the smallest number possible and that in the considered transformations there should be no question of splitting the "components".

The quantity of the  $\nu$ -th component in the  $\kappa$ -th phase will be denoted by  $m_{\nu}^{(\kappa)}$ . If, however, an arbitrary phase or component be referred to, the corresponding index will be omitted.

To begin with, we will apply the method of free energy and we thus have to make the sum

$$\Psi^{(1)} + \Psi^{(2)} + . . . . + \Psi^{(k)}$$

a minimum, keeping the total volume

$$V = v^{(1)} + v^{(2)} + . . . . + v^{(k)}$$

constant and treating each  $\Psi$ , at a given temperature, as a function of the corresponding  $v$  and of  $m_1, m_2, . . . m_n$ .

It is enough to consider a few special infinitesimal changes of the state. In the first place, as in the case of two phases, we can allow the volume of one phase to increase infinitesimally and that of another phase to decrease as much without altering any of the magnitudes  $m$ . Let, for instance,  $v^{(1)}$  and  $v^{(2)}$  alone vary, so that

$$\delta v^{(2)} = -\delta v^{(1)}.$$

The condition

$$\frac{\partial \Psi^{(1)}}{\partial v^{(1)}} \delta v^{(1)} + \frac{\partial \Psi^{(2)}}{\partial v^{(2)}} \delta v^{(2)} = 0$$

will then lead to the equation

$$\frac{\partial \Psi^{(1)}}{\partial v^{(1)}} = \frac{\partial \Psi^{(2)}}{\partial v^{(2)}} \quad . \quad . \quad . \quad . \quad (107)$$

or

$$p^{(1)} = p^{(2)}.$$

Thus we find, which we already knew, that the pressure must have in all phases the same value  $p$ .

In the second place, keeping all  $v$ 's constant, we can allow an infinitesimal quantity of one of the components to pass from one phase to another. If, *e.g.*, the first phase gives up an infinitesimal quantity  $\omega$  of the first component to the second phase,  $\Psi^{(1)}$  changes by  $-\frac{\partial \Psi^{(1)}}{\partial m_1^{(1)}}\omega$  and  $\Psi^{(2)}$  by  $\frac{\partial \Psi^{(2)}}{\partial m_1^{(2)}}\omega$ , so that the condition  $\Sigma \delta \Psi^{(k)} = 0$  gives the equation

$$\frac{\partial \Psi^{(1)}}{\partial m_1^{(1)}} = \frac{\partial \Psi^{(2)}}{\partial m_1^{(2)}} \quad . \quad . \quad . \quad . \quad (108)$$

This may be referred to as the equilibrium condition for the first two phases with respect to the first component.

A similar equation will hold for every pair of phases with respect to each component contained in them, and it will readily be seen that in this way all the equilibrium conditions are obtained.

83. The results just derived lead to an important conclusion. The equilibrium condition for the first component is, for the first and the third phases,

$$\frac{\partial \Psi^{(1)}}{\partial m_1^{(1)}} = \frac{\partial \Psi^{(3)}}{\partial m_1^{(3)}},$$

and for the second and the third phases,

$$\frac{\partial \Psi^{(2)}}{\partial m_1^{(2)}} = \frac{\partial \Psi^{(3)}}{\partial m_1^{(3)}}.$$

From these two equations follows (108). Thus, if of three phases having a component in common the first is in equilibrium with the third with respect to this component and also the second with the third, so also is the first with the second. The proof may also be restated as follows. The equilibrium between the first and the second phases implies that the free energy does not change when an infinitesimal quantity of a given component

passes from the first to the second phase. Now, this process can be imagined to take place in two stages, the quantity in question passing first from the first to the third and then from the third to the second phase. The free energy will thus not change, since it remains constant in each stage.

A simple example of this kind is afforded by bodies which can give off steam. Two phases, *c.g.*, a salt containing water and a saturated solution of this salt, while coexisting with each other, can be in equilibrium with the same vapour phase.

84. If one wishes to treat the problem of equilibrium by the method of the thermodynamical potential, one has to assume that the pressure has in all parts of the system the same value  $p$  and to consider  $\zeta$  for each phase as a function of  $p, T$ , and  $m_1, m_2, \dots$ , the quantities of the components in that phase. Then, allowing an infinitesimal quantity of a component to pass, at constant  $p$  and  $T$ , from one phase into another, one obtains the equilibrium conditions in much the same form as (108). Thus, for instance, the equilibrium between the first and second phase with respect to the first component will be expressed by the equation

$$\frac{\partial \zeta^{(1)}}{\partial m_1^{(1)}} = \frac{\partial \zeta^{(2)}}{\partial m_1^{(2)}} \quad . \quad . \quad . \quad . \quad (109)$$

The identity of this formula with (108) can be readily verified. Let us recall that  $\Psi$  for each phase was considered as a function of  $v, T, m_1, m_2, \dots$ , and that the derivative of  $\Psi$  with respect to one of the  $m$ 's in formula (108) had to be taken not only for constant values of the remaining  $m$ 's and the temperature, but also for a constant volume  $v$ , which can be expressed by writing

$$\left( \frac{\partial \Psi}{\partial m} \right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (110)$$

On the other hand, we now have derivatives at constant pressure, *i.e.*

$$\left( \frac{\partial \zeta}{\partial m} \right)_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (111)$$

Introducing, however, in  $\Psi$ , instead of  $v$ , the pressure  $p$  as independent variable, the derivative  $\left( \frac{\partial \Psi}{\partial m} \right)_p$  can be formed.

This is connected with the derivative (110) by

$$\left(\frac{\partial \Psi^*}{\partial m}\right)_p = \left(\frac{\partial \Psi^*}{\partial m}\right)_v + \left(\frac{\partial \Psi^*}{\partial v}\right)_m \left(\frac{\partial v}{\partial m}\right)_p,$$

where in  $\left(\frac{\partial \Psi}{\partial v}\right)_m$  all  $m$ 's are kept constant, so that this derivative has the value  $-p$ , and

$$\left(\frac{\partial \Psi^*}{\partial m}\right)_p = \left(\frac{\partial \Psi^*}{\partial m}\right)_v - p \left(\frac{\partial v}{\partial m}\right)_p.$$

Now,

$$\zeta = \Psi^* + pv,$$

and therefore,

$$\left(\frac{\partial \zeta}{\partial m}\right)_p = \left(\frac{\partial \Psi^*}{\partial m}\right)_p + p \left(\frac{\partial v}{\partial m}\right)_p.$$

This proves the equality of (110) and (111). We thus see that the magnitudes appearing in the conditions of equilibrium (108) and (109) are exactly the same.

85. Let us now seek to determine the number of mutually independent conditions of equilibrium, and let us see what can be derived from it. For this purpose we note that for a given  $T$  the free energy of a phase is a homogeneous function of the first degree in  $v, m_1, m_2, \dots$ , and that for constant  $T$  and  $p$  the thermodynamical potential is again such a function of  $m_1, m_2, \dots$ . In fact, a certain phase being given, we can imagine another for which  $p$  and  $T$  have the same values, but  $v, m_1, m_2, \dots$ ,  $\Psi$ , and  $\zeta$  are  $n$  times as great. Whence it follows that all derivatives such as  $\partial \Psi / \partial v$ ,  $\partial \Psi / \partial m$  can be expressed by the ratios

$$\frac{m_1}{v}, \frac{m_2}{v}, \dots \quad (112)$$

*i.e.* by the partial densities of the components. Likewise, all the derivatives  $\partial \zeta / \partial m$  depend on the ratios

$$\frac{m_2}{m_1}, \frac{m_3}{m_1}, \dots \quad (113)$$

We have further to take into account that there may be phases in which some components do not occur at all and into which they cannot be taken up. The existence of such phases will manifestly reduce the number of equilibrium conditions of the form (108) or (109).

To come at once to the general case let us suppose that the first component occurs in  $k_1$  phases, the second in  $k_2$  phases, etc. We have then for the equilibrium with respect to the first component  $k_1 - 1$  mutually independent equations of the form (108), similarly  $k_2 - 1$  equations expressing the equilibrium with respect to the second component, and so on. And since there are also  $k - 1$  mutually independent conditions of the form (107), we have in all

$$a = k - 1 + k_1 - 1 + k_2 - 1 + \dots + k_n - 1 \\ - k + k_1 + k_2 + \dots + k_n = (n + 1)$$

equations between the derivatives of  $\Psi$  with respect to  $v$  and  $m$ . Now, if the first phase contains  $n^{(1)}$ , the second  $n^{(2)}$  components, etc., the number of partial densities (112) is

$$b = n^{(1)} + n^{(2)} + \dots + n^{(k)},$$

instead of which we may write

$$b = k_1 + k_2 + \dots + k_n.$$

Thus, if  $k = n + 1$ , *i.e.* if the number of phases is by one greater than that of components, we have as many equations as unknowns. For a given temperature, therefore, all partial densities as well as the pressure which depends on them will be completely determined. The temperature can still be chosen arbitrarily. If it be increased or decreased, we have equilibrium at another pressure and with modified phase compositions corresponding to the new temperature. If  $k = n + 2$ , then  $a = b + 1$ , and the equations can no longer be satisfied for an arbitrarily chosen temperature; equilibrium between  $n + 2$  phases is possible only at a certain temperature which, together with the partial densities, will be completely determined by the equations.

In the case of the system water-steam, or water-ice,  $n = 1$ ,  $k = 2$ ; an example in which  $n = 2$ ,  $k = 3$  we have in the co-existence of a salt containing water, its aqueous solution, and steam. In these cases equilibrium is possible at different temperatures, though only at a determined pressure. On the other hand, water, ice, and steam, or two solid hydrates of a salt, its solution, and steam can coexist only at a certain temperature.

The same conclusions can be arrived at by means of the thermodynamical potential. We then have

$$a' = k_1 + k_2 + \dots + k_n - n$$

equations of the form (109) and these contain, apart from  $p$  and  $T$ , the ratios (113) of which there are

$$b' = n^{(1)} - 1 + n^{(2)} - 1 + \dots + n^{(k)} - 1 = k_1 + k_2 + \dots + k_n - k$$

mutually independent ones. If  $k = n + 1$ , and therefore  $a' = b' + 1$ , then at a given temperature all these ratios as well as the pressure can be found from the equations. If the number of phases is by two greater than that of components, so that  $a' = b' + 2$ , then also the temperature is determined.

$n$  substances which distribute themselves over less than  $n + 1$  phases can form, at a given temperature, a plurality of equilibria differing from each other in pressure as well as in density and composition of the several phases. In such cases, however, the state is completely determined, provided  $T$  and  $p$  are chosen and the total quantity of each component is known. For the latter gives  $n$  equations between the magnitudes  $m$ , so that we have in all

$$a' + n = k_1 + k_2 + \dots + k_n$$

equations, which coincides with the number of the magnitudes  $m$ , viz.

$$n^{(1)} + n^{(2)} + \dots + n^{(k)}.$$

Similarly it can be shown that the state of a system comprising less than  $n + 1$  phases is determined, if it be known how much it contains of each component and what space it occupies at a given temperature.

86. The actual solution of the preceding equations is, in general, impossible since the form of the functions  $\Psi$  and  $\zeta$  cannot be determined. But some quantitative and experimentally verifiable results can be obtained by comparing two states of equilibrium which differ from each other very little. In one of these states, to be called the *first*, let  $n + 1$  phases consisting of  $n$  components  $A$  be in equilibrium with one another at the temperature  $T$  and the pressure  $p$ . Let the *second* state differ from the first inasmuch as the temperature and pressure are  $T' + \delta T$  and  $p + \delta p$  and a small quantity of a new component  $C$  has been added to the system, of which the phases receive



$c^{(1)}, c^{(2)}, \dots, c^{(n+1)}$  units. The latter magnitudes as well as  $\delta T$  and  $\delta p$  will be considered as infinitesimals of the same order.

To begin with we notice that, as regards the first state,  $n+1$  numbers  $\alpha^{(1)}, \alpha^{(2)}, \dots, \alpha^{(n+1)}$  can be assigned whose ratios are determined by the equations

$$\left. \begin{aligned} \alpha^{(1)}m_1^{(1)} + \alpha^{(2)}m_1^{(2)} + \dots + \alpha^{(n+1)}m_1^{(n+1)} &= 0 \\ \alpha^{(1)}m_n^{(1)} + \alpha^{(2)}m_n^{(2)} + \dots + \alpha^{(n+1)}m_n^{(n+1)} &= 0, \end{aligned} \right\} \quad (114)$$

where some of the coefficients may vanish. The numbers  $\alpha$  will, of course, be partly positive and partly negative. Let the first  $r$  numbers be positive and the remaining ones negative. Then, as will appear from (114), a transformation is possible in which, while the temperature, the pressure, the density, and the composition of each phase are unaltered, the quantities of the first  $r$  phases increase at the expense of the remaining ones. We determine this transformation by requiring that the quantity of each phase should change in the ratio of 1 to  $1 + a\omega$ , where  $a$  is the number corresponding to the phase in question and  $\omega$  an infinitesimal constant.

The thermodynamical potential of each phase will change in the same ratio. The total thermodynamical potential will, therefore, change by

$$\{\alpha^{(1)}\zeta^{(1)} + \alpha^{(2)}\zeta^{(2)} + \dots + \alpha^{(n+1)}\zeta^{(n+1)}\}\omega,$$

and since this must vanish, we have the equation

$$\alpha^{(1)}\zeta^{(1)} + \alpha^{(2)}\zeta^{(2)} + \dots + \alpha^{(n+1)}\zeta^{(n+1)} = 0, \quad (115)$$

which might also be readily derived from the equilibrium conditions given in Art. 84 in conjunction with the equations (114). For this purpose it would be enough to notice that since the thermodynamical potential is, by Art. 85, a homogeneous function of the first degree of  $m_1, m_2, \dots, m_n$ , we have, for each phase,

$$\zeta = m_1 \frac{\partial \zeta}{\partial m_1} + m_2 \frac{\partial \zeta}{\partial m_2} + \dots + m_n \frac{\partial \zeta}{\partial m_n}.$$

As regards the second state, let  $m_1^{(1)}, m_1^{(2)}$ , etc., differing infinitesimally from  $m_1^{(1)}, m_1^{(2)}$ , etc., denote the quantities of the components  $A$  occurring in the several phases, and  $\alpha^{(1)}, \alpha^{(2)}$ ,

etc.  $n+1$  numbers differing infinitesimally from  $a^{(1)}$ ,  $a^{(2)}$ , etc., and satisfying the equations

$$\left. \begin{aligned} \bar{\alpha}^{(1)}\bar{m}_1^{(1)} + \bar{\alpha}^{(2)}\bar{m}_1^{(2)} + \dots + \bar{\alpha}^{(n+1)}\bar{m}_1^{(n+1)} &= 0 \\ \bar{\alpha}^{(1)}\bar{m}_n^{(1)} + \bar{\alpha}^{(2)}\bar{m}_n^{(2)} + \dots + \bar{\alpha}^{(n+1)}\bar{m}_n^{(n+1)} &= 0. \end{aligned} \right\} \quad (116)$$

We will subject this state also to an infinitesimal change at constant temperature and pressure and equate to zero the corresponding variation of the thermodynamical potential. Let this change consist in varying the quantities of all components  $A$  in each phase in the ratio of 1 to  $1+a\omega$ , while the quantity of  $C$  remains unaltered.

Since the quantities of the former components contained in an arbitrary phase will then increase by  $\bar{a}\omega\bar{m}_1$ ,  $\bar{a}\omega\bar{m}_2$ ,  $\dots$   $\bar{a}\omega\bar{m}_n$ , the change of the thermodynamical potential, say  $\xi$ , will be

$$\bar{a}\omega\left(\bar{m}_1\frac{\partial\bar{\xi}}{\partial\bar{m}_1} + \bar{m}_2\frac{\partial\bar{\xi}}{\partial\bar{m}_2} + \dots + \bar{m}_n\frac{\partial\bar{\xi}}{\partial\bar{m}_n}\right). \quad (117)$$

Since  $\bar{\xi}$  is a homogeneous function of the first degree in  $\bar{m}_1$ ,  $\bar{m}_2$ ,  $\dots$   $\bar{m}_n$  and  $c$ , we have

$$\bar{m}_1\frac{\partial\bar{\xi}}{\partial\bar{m}_1} + \bar{m}_2\frac{\partial\bar{\xi}}{\partial\bar{m}_2} + \dots + \bar{m}_n\frac{\partial\bar{\xi}}{\partial\bar{m}_n} + c\frac{\partial\bar{\xi}}{\partial c} = \bar{\xi},$$

so that (117) can be written

$$\bar{a}\omega\left(\bar{\xi} - c\frac{\partial\bar{\xi}}{\partial c}\right).$$

Now, since

$$\xi = \Psi + pv,$$

it is manifest that, as was proved for  $\Psi$  in Art. 74, so also in  $\xi$  the variable  $x$ , or in our case  $c$ , occurs explicitly only in the term

$$RT\{c \log c + (1-c) \log (1-c)\}.$$

Since  $c$  is assumed to be very small, we can write

$$\xi = \xi_0 + ac + \beta c^2 + \dots + RT\{c \log c + (1-c) \log (1-c)\},$$

where  $\xi_0$  is the value of  $\bar{\xi}$  for  $c=0$ . Thus,

$$\bar{\xi} - c\frac{\partial\bar{\xi}}{\partial c} = \xi_0 + RT \log (1-c) = \xi_0 - RTc,$$

so that, ultimately, (117) can be written

$$\bar{a}\omega(\xi_0 - RTc). \quad (118)$$

Forming similar expressions for each phase and equating to zero the variation of the total thermodynamical potential, we have

$$\Sigma a \zeta_0 - RT \Sigma \bar{a} c = 0. \quad (119)$$

87. This equation in which the sums extend to the  $n+1$  phases has now to be compared with formula (115), which can be written

$$\Sigma a \zeta = 0.$$

For this purpose we subtract this equation from (119). As was already done in the case of  $p$  and  $T$  we denote the infinitesimal variation of a magnitude in passing from the first to the second state of equilibrium by  $\delta$ . Thus, we write  $\delta m$  for the difference  $\bar{m} - m$  of two corresponding values of  $m$ , similarly  $\delta a$  for  $\bar{a} - a$ , while  $\delta \zeta$  will stand for  $\zeta_0 - \zeta$ . Since  $c$  is infinitesimal, the coefficient  $a$  in the last term of (119) can be replaced by the corresponding  $a$ . The result thus becomes

$$\delta \Sigma a \zeta - RT \Sigma a c = 0$$

$$\text{or} \quad \Sigma a \delta \zeta + \Sigma \zeta \delta a - RT \Sigma a c = 0. \quad (120)$$

Now,

$$\delta \zeta = \frac{\partial \zeta}{\partial m_1} \delta m_1 + \frac{\partial \zeta}{\partial m_2} \delta m_2 + \dots + \frac{\partial \zeta}{\partial m_n} \delta m_n + \frac{\partial \zeta}{\partial T} \delta T + \frac{\partial \zeta}{\partial p} \delta p,$$

where  $\partial \zeta / \partial m_1$ , etc. have the values belonging to the first state of equilibrium. Substituting this in (120) we notice that for each phase  $-\partial \zeta / \partial T$  and  $\partial \zeta / \partial p$  represent the entropy  $\eta$  and the volume  $v$ , that,  $m$  being the quantity of any of the components  $A$ , the derivative  $\partial \zeta / \partial m$  has, by Art. 84, the same value for all phases, further, that for each component, by (114) and (116),

$$\delta \Sigma a m = 0 \quad \text{or} \quad \Sigma a \delta m = -\Sigma m \delta a,$$

and, finally, that  $\zeta$  is a homogeneous function of the first degree of  $m_1, m_2, \dots, m_n$ . Taking account of all this we find that  $\Sigma a \delta \zeta$  is the sum of

$$-\Sigma (a \eta) \delta T + \Sigma (a v) \delta p$$

and of

$$\begin{aligned} \frac{\partial \zeta}{\partial m_1} \Sigma a \delta m_1 + \dots + \frac{\partial \zeta}{\partial m_n} \Sigma a \delta m_n &= -\frac{\partial \zeta}{\partial m_1} \Sigma m_1 \delta a - \dots - \frac{\partial \zeta}{\partial m_n} \Sigma m_n \delta a \\ &= -\Sigma \left[ m_1 \frac{\partial \zeta}{\partial m_1} + \dots + m_n \frac{\partial \zeta}{\partial m_n} \right] \delta a = -\Sigma \zeta \delta a. \end{aligned}$$

Ultimately, therefore, equation (120) becomes

$$-\Sigma(a\eta)\delta T + \Sigma(av)\delta p - RT\Sigma ac = 0. \quad . \quad . \quad (121)$$

88. The sums appearing in this equation have a simple meaning. Imagine a transformation (Art. 86) in which  $a^{(1)}$ ,  $a^{(2)}$ ,  $a^{(3)}$ ,  $\dots$   $a^{(r)}$  times the quantities of the first  $r$  phases present in the first state of equilibrium arise from  $-a^{(r+1)}$ ,  $\dots$   $-a^{(n+1)}$  times the quantities of the remaining phases. In this transformation, supposed to take place at constant temperature and pressure, the volume of the system increases by  $\Delta v = \Sigma av$ , and the entropy by  $\Delta \eta = \Sigma a\eta$ . The process being reversible we can as well say that  $\Sigma a\eta$  is the heat  $\Delta Q$  to be supplied to the system, divided by  $T$ . As regards the meaning of  $\Sigma ac$ , suppose that the above transformation, determined by the numbers  $a$ , takes place also in the second case in which the system contains the new component  $C$ . Then, if the value of  $c$  is to remain unaltered for each phase, a certain quantity of the component  $C$  must be supplied to the system, and this quantity is just given by  $\Sigma ac$ .

89. From the last obtained equation a number of different conclusions can be derived. In the first place we can assume that the component  $C$  is missing also in the second state. Then the equation reduces to a known relation between the simultaneous changes of temperature and pressure of  $n + 1$  phases in equilibrium. Such, *e.g.*, is the relation which holds between vapour pressure and temperature or freezing point and pressure.

In the second place we can investigate the effect produced upon the equilibrium by a small quantity of the new component  $C$ , assuming for simplicity that either  $\delta T$  or  $\delta p$  is zero. Let, *e.g.*, in a liquid  $A$  which is in contact with its vapour an infinitesimal quantity of a substance  $C$  be dissolved. Call the vapour the first, and the liquid the second phase, and let the transformation consist in the evaporation of a mass unit of liquid. If the vapour and the liquid contain, each per unit mass of  $A$ , the quantities  $n^{(1)}$  and  $n^{(2)}$  of the substance  $C$ , then  $\Sigma ac = n^{(1)} - n^{(2)}$ , and if the specific volumes are  $w^{(1)}$  and  $w^{(2)}$ , we have  $\Sigma av = w^{(1)} - w^{(2)}$ . Thus, assuming that  $\delta T = 0$ ,

$$\delta p = RT \frac{n^{(1)} - n^{(2)}}{w^{(1)} - w^{(2)}},$$

and if the dissolved substance does not evaporate,

$$\delta p = -RT \frac{n^{(2)}}{w^{(1)} - w^{(2)}}. \quad (122)$$

This is the known formula for the lowering of vapour pressure produced by dissolving a foreign substance in a liquid.

With equal ease the similar displacement of the freezing point can be deduced from the general equation. In this case we assume that the substance  $A$  occurs partly in the solid and partly in the liquid state, and call the solid the first phase. We now put  $\delta p = 0$  and leave to  $n^{(1)}$ ,  $n^{(2)}$ ,  $w^{(1)}$ ,  $w^{(2)}$  their previous meaning, referring, however, the index (1) to the solid phase. Let, further,  $r$  be the heat of melting per mass unit, expressed in mechanical units. Then  $\sum a\eta = -\frac{r}{T}$ , and

$$\delta T = \frac{RT^2}{r} (n^{(1)} - n^{(2)}).$$

In particular, if the component  $C$  does not occur in the solid phase, the formula is simplified to

$$\delta T = -\frac{RT^2 n^{(2)}}{r}. \quad (123)$$

90. The subject of the preceding articles calls for some remarks.

In the first place let us notice that we can compare with each other the values of the free energy, or the entropy, or the thermodynamical potential, only for different states of one and the same system but not for entirely different systems. In this connection it may at first sight seem strange that our formulæ contain derivatives such as  $\partial\Psi/\partial m$  and  $\partial\xi/\partial m$ . In fact, to differentiate the free energy  $\Psi$  of a phase with respect to the quantity  $m$  of one of the components contained in it is the same thing as to compare the values of  $\Psi$  for two phases containing the quantities  $m$  and  $m + dm$ , and thus for two systems which do not consist of the same amounts of a substance. But looking into the matter more closely, it will be seen that we were actually comparing only the values of the free energy for different states of one and the same quantity of substance ;

for we were always concerned with the change of the total value of  $\Psi$  for a system composed of several phases, and against the concept of viewing this value before as well as after such a change as the sum of a number of terms belonging to different phases nothing can be objected.

In the second place let us recall that into the expressions of the energy  $\epsilon$  and the entropy  $\eta$  additive constants  $C$  and  $C'$  can always be included whose values remain undetermined and that, therefore, to the value of the free energy a term  $C - TC'$  can always be added. We have avoided such terms by choosing a certain state in which the free energy should have the value zero. But even if we had not done so, the undetermined constants would, clearly, be absent in all our final formulæ. For, as we know, these constants can have no influence upon the difference of the values of  $\Psi$  for different states at the same temperature.

91. *Dissociation of a gas.*—Let us now consider briefly the dissociation of a gas and let us see how this problem can be treated by the method of thermodynamics.

We will suppose that the gas can split into two components and that there is besides a certain quantity of either component. Let there be  $n_1$  gram molecules of the first gas  $A$  of molecular weight  $M_1$ , and let  $n_2$  and  $M_2$ ,  $N$  and  $\alpha M_1 + \beta M_2$  have similar meanings for the second gas  $B$  and for the compound  $C$  of the two gases.

Let the mixture be contained in a vessel of invariable volume  $v$ , and let  $T$  denote its temperature. The equilibrium can be determined by the condition that the free energy of the whole system shall be a minimum.

Let the energy per gram molecule of the gas  $A$  at the volume  $v/n_1$  and temperature  $T$  be

$$\epsilon_1 + c_1 T,$$

and therefore the entropy, by Art. 31,

$$\eta_1 + c_1 \log T + R \log \frac{v}{n_1},$$

where  $\epsilon_1$  and  $\eta_1$  are constants.

Similar expressions (with  $\epsilon_2$ ,  $\eta_2$ ,  $c_2$  and  $E$ ,  $H$ ,  $C$ ) can be written down for the energy and the entropy of the gases  $B$



and  $C$ .  $R$  is the general gas constant. Thus, by the theorem proved in Art. 70, the total free energy of the system will be

$$\begin{aligned}
 & -T \left\{ n_1 \left( \eta_1 + c_1 \log T + R \log \frac{v}{n_1} \right) + n_2 \left( \eta_2 + c_2 \log T + R \log \frac{v}{n_2} \right) \right. \\
 & \quad \left. + N \left( H + C \log T + R \log \frac{v}{N} \right) \right\} \\
 & + n_1(\epsilon_1 + c_1 T) + n_2(\epsilon_2 + c_2 T) + N(E + CT).
 \end{aligned}$$

The variables  $N$ ,  $n_1$ , and  $n_2$  are not independent of each other. If  $N$  increases by  $\delta N$ , then

$$\delta n_1 = -\alpha \delta N \quad \text{and} \quad \delta n_2 = -\beta \delta N.$$

Thus  $N$  can be taken as the only independent variable, and the condition that the variation of the free energy, corresponding to an increase of  $N$  by  $\delta N$ , shall be zero will give the equation

$$\begin{aligned}
 & -\alpha(\epsilon_1 + c_1 T) - \beta(\epsilon_2 + c_2 T) + (E + CT) \\
 & -T \left\{ -\alpha \left( \eta_1 + c_1 \log T + R \log \frac{v}{n_1} \right) - \beta \left( \eta_2 + c_2 \log T + R \log \frac{v}{n_2} \right) \right. \\
 & \quad \left. + \left( H + C \log T + R \log \frac{v}{N} \right) + (\alpha + \beta - 1)R \right\} = 0.
 \end{aligned}$$

Let us denote the sum of the three constant terms not containing  $T$  by  $P$ , further, the constant part of the coefficient of  $T$  by  $Q$ , and the coefficient of  $T \log T$  by  $S$ . Then the equilibrium condition will assume the form

$$P + QT + ST \log T + RT \log \frac{v^{\alpha+\beta-1}}{n_1^\alpha n_2^\beta N^{-1}} = 0. \quad (124)$$

Our aim is thus attained, since this equation can be solved for  $n_1^\alpha n_2^\beta N^{-1}$  as a function of  $T$  and  $v$ . If the constants  $P, Q, S$  and the total quantities of the gases  $A$  and  $B$  are given, the state of the system can be completely determined. For then  $n_1 + Na$ ,  $n_2 + N\beta$ , and  $n_1^\alpha n_2^\beta / N$  are known, whence  $n_1$ ,  $n_2$ , and  $N$  can be found.

From (124) we see at once how the dissociation varies when at constant temperature the volume is increased or diminished. In fact,  $n_1^\alpha n_2^\beta / N$  will then change proportionally to  $v^{\alpha+\beta-1}$ .

The degree of dissociation will not be affected by the volume of the vessel if  $\alpha + \beta = 1$ , that is to say, if the number of molecules

is not altered by the dissociation. If, however, the number of molecules increases in the process of dissociation, *i.e.* if  $\alpha + \beta > 1$ , then  $n_1^\alpha n_2^\beta / N$  will increase with the volume which can take place only if  $n_1$  and  $n_2$  increase at the expense of  $N$ . In this case then the dissociation will be increased by increasing the volume.

92. We come at length to speak of the graphical representation which was used by van der Waals in his important investigations on gaseous and liquid mixtures, the so-called  $\Psi$ -surface of van der Waals.

The temperature being kept constant, the free energy per gram molecule is a function of the composition of the mixture ( $x$ ) and its volume  $v$ . This function is given by formula (81) or (82).

Let now  $x$  and  $v$  be represented by the rectangular co-ordinates in a horizontal plane, and the value of  $\Psi$  for the phase in question by the third co-ordinate of a space point.

Since the values of  $x$  lie between 0 and 1, the  $\Psi$ -surface will be enclosed between two parallel vertical planes, *viz.* the planes  $x=0$  and  $x=1$ . On the third side it will be limited by the vertical plane  $v=0$ , while in the direction of the  $v$ -axis it extends to infinity. In order to investigate the shape of the  $\Psi$ -surface we will consider its sections by vertical planes of constant  $x$ . The last term of (81) or (82) is now constant and, keeping henceforth to formula (81), we have only to investigate

$$\Psi' = -\frac{a}{v} - RT \log (v - b).$$

Now, 
$$\frac{\partial \Psi'}{\partial v} = \frac{a}{v^2} - \frac{RT}{v - b} = -p.$$

Thus, the pressure taken with the negative sign gives the trigonometrical tangent of the angle which the  $\Psi'$ -line makes with the  $v$ -axis.

To see how at constant temperature the pressure varies with the volume we make use of the isothermals in the  $pv$ -diagram for a mixture. According to van der Waals' theory these isothermals have the same form as those for a simple substance. (The latter, which are assumed to be known, are represented on Fig. 21.) In fact, the equation of state for mixtures has

the same form as for simple substances, with the values of the parameters (cf. Art. 73)

$$a = (1-x)^2 a_1 + 2x(1-x) a_{12} + x^2 a_2$$

$$b = (1-x)^2 b_1 + 2x(1-x) b_{12} + x^2 b_2.$$

There exists thus for a mixture also a *critical isothermal* which has an inflexion point (*B*) with a horizontal tangent, the co-ordinates of this point being the critical pressure and the critical volume.

For this point

$$\frac{\partial p}{\partial v} = 0 \quad \text{and} \quad \frac{\partial^2 p}{\partial v^2} = 0,$$

$$i.e. \quad \frac{2a}{v^3} - \frac{RT}{(v-b)^2} = 0 \quad \text{and} \quad -\frac{6a}{v^4} + \frac{2RT}{(v-b)^3} = 0,$$

$$\text{whence} \quad v = v_k = 3b \quad \text{and} \quad RT = RT_k = \frac{8}{27} \frac{a}{b}.$$

The temperature  $T_k$  thus determined is called the critical temperature of the mixture. As a matter of fact, this is nothing more than a definition of the critical temperature.

The coincidence of two phases as to their properties, which for simple substances takes place at the critical temperature, is replaced in the case of mixtures by a less simple behaviour.

The temperature  $T_k$  for a mixture, as expressed by the last formula, depends in a rather complicated way on  $x$ ; it can attain a maximum for one or more values of  $x$ . In most cases, however,  $T_k$  will either decrease or increase continually

when  $x$  varies from 0 to 1. With regard to the form of the  $\Psi v$ -section of the  $\Psi$ -surface three cases can be distinguished \* :

1°.  $T > T_k$ .

$$\frac{\partial^2 \Psi}{\partial v^2} = -\frac{\partial p}{\partial v} \text{ is always positive.}$$

\*  $\partial \Psi / \partial v = -p$  is always negative, apart from some cases of negative pressure, when the derivative is positive and the  $\Psi v$ -line rises with increasing  $v$ .

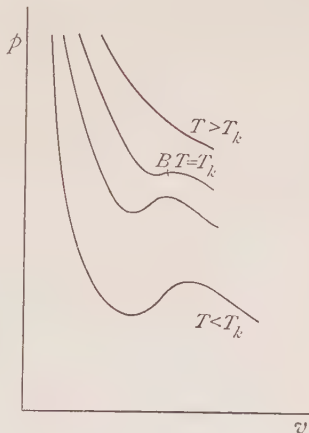


FIG. 21.

The  $\Psi v$ -line has thus no inflexion point and turns its convex side always downwards.

2°.  $T < T_k$  (cf. Fig. 22).

$\frac{\partial^2 \Psi}{\partial v^2} = -\frac{\partial p}{\partial v}$  is negative between  $B$  and  $C$ , positive outside this

interval, and nil at the points  $B$  and  $C$ . Thus the  $\Psi v$ -curve has two inflexion points, at  $B$  and  $C$ , and forms a bend.

3°.  $T = T_k$ .

$\frac{\partial^2 \Psi}{\partial v^2} = -\frac{\partial p}{\partial v}$  is everywhere positive except at the critical point,

where  $\partial p / \partial v$  is nil. Here also  $\partial^2 p / \partial v^2 = 0$ , and therefore

$\partial^3 \Psi / \partial v^3 = 0$ , so that the tangent at the critical point has four points in common with the  $\Psi v$ -curve. For very large  $v$  this curve becomes almost horizontal, since  $p$  is then very small. On the other hand, for very small  $v$ ,  $p$  is large and the  $\Psi v$ -curve becomes almost vertical.  $\Psi$  itself is then very large and positive, as will be seen by assuming  $v$  in the second term of (81)

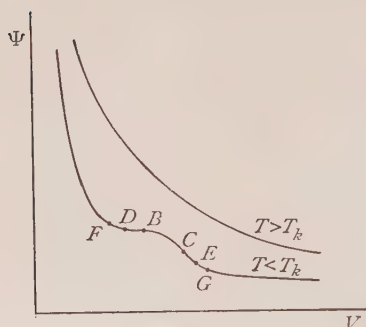


FIG. 22.

but little greater than  $b$ . In Fig. 22 two such  $\Psi v$ -lines are drawn.

93. The shape of the  $\Psi$ -surface will depend on the choice of the temperature for which it is constructed. If this is higher than the critical temperatures of mixtures of every possible composition, none of the  $\Psi v$ -lines forms a bend, and the surface has, therefore, no plait in the direction of the  $x$ -axis (no "transversal plait"). If the temperature lies below the lowest critical temperature of the mixtures, a transversal plait runs across the whole surface, from  $x=0$  to  $x=1$ . Finally, if the temperature lies between two critical temperatures, which is the most interesting case, there is a transversal plait stretching over a part of the surface. Here again different sub-cases are possible, according as the critical temperature of the mixtures varies between  $x=0$  and  $x=1$  monotonously or attains a maximum

or minimum. In the former case the plait has an end-point upon the surface, while in the latter case the temperature can be so chosen that the plait shall occur in the middle, not at the edge of the surface (if  $T_k$  has a maximum) or *vice versa* (if  $T_k$  has a minimum).

94. Next, to determine the form of the sections of the surface by planes of constant volume, *i.e.* of the  $\Psi x$ -sections, we have to write down the derivative of  $\Psi$  with respect to  $x$ . This is, by formula (81),

$$\frac{\partial \Psi}{\partial x} = -\frac{1}{v} \frac{da}{dx} + \frac{RT}{v-b} \frac{db}{dx} + RT \log \frac{x}{1-x}.$$

When  $x$  approaches 1 or 0, the last term tends to  $\pm\infty$ , while between these extremes  $\partial \Psi / \partial x$  certainly vanishes somewhere. Thus the  $\Psi x$ -sections are tangential to the planes  $x=0$  and  $x=1$ . In other words, the latter are tangential planes of the  $\Psi$ -surface. Again,

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{1}{v} \frac{d^2 a}{dx^2} + \frac{RT}{(v-b)^2} \left( \frac{db}{dx} \right)^2 + \frac{RT}{v-b} \frac{d^2 b}{dx^2} + RT \left( \frac{1}{x} + \frac{1}{1-x} \right). \quad (125)$$

If the  $\Psi x$ -curves turn everywhere their convex side downwards, there can be no question of a plait in the direction of the  $v$ -axis ("longitudinal plait"). The existence of such a plait will thus depend on the sign of  $\partial^2 \Psi / \partial x^2$ . If  $x$  is nearly 0 or 1, the last term of (125), which is always positive, will decide the question. Somewhere between these values  $\partial^2 \Psi / \partial x^2$  may become negative. From the values of  $a$  and  $b$  (Art. 92) follows

$$\frac{d^2 a}{dx^2} = 2a_1 - 4a_{12} + 2a_2$$

and

$$\frac{d^2 b}{dx^2} = 2b_1 - 4b_{12} + 2b_2.$$

Thus the sign of  $\partial^2 \Psi / \partial x^2$  for given  $x$  and  $v$  will depend on the values of the six coefficients  $a_1$ ,  $a_{12}$ , etc., and, as we shall see presently, these will decide at the same time whether or not two substances can mix with each other in all proportions. In fact, if  $\partial^2 \Psi / \partial x^2$  is always positive and the  $\Psi x$ -curve has no bend, the substances cannot split under diminution of free energy.

We have already met with similar considerations in the case of the  $\zeta$ -surface, and shall return to them presently with a view to the  $\Psi$ -surface.

From (125) we see that a large value of  $a_{12}$  favours mixing, while large values of  $a_1$  and  $a_2$  are favourable to splitting. On the other hand a high value of  $b_{12}$  will be conducive to splitting and high values of  $b_1$  and  $b_2$  will promote mixing. All this becomes obvious by recalling the significance of these coefficients. In fact, two substances will easily mix if they strongly attract each other, that is to say, if  $a_{12}$  is large. When  $v$  increases, this reasoning is put to the background, for then the last term of (125) becomes decisive; thus, at a large volume every pair of substances can mix perfectly.

If  $\partial^2\Psi/\partial x^2$  can assume negative values, the surface has a longitudinal plait, *i.e.* in the direction of the  $v$ -axis. It appears that such is mostly the case with abnormal substances which do not obey the law of corresponding states. That this phenomenon does not occur in normal substances seems hard to explain. There is nothing in normal substances to prevent us from expecting such a plait. At any rate, we shall in the sequel limit ourselves to transversal plaits, leaving on one side the existence of a longitudinal plait, *i.e.* the inability of substances to mix in all proportions.

95. Let us now see what is necessary for a phase to be stable, *i.e.* not to split into two or more others. To answer this question we will make use of some properties of the  $\Psi$ -surface, which agree with those of the  $\zeta$ -surface (Art. 58) and can readily be proved in a similar way.

The first of these properties is that, if  $A$  and  $B$  be two points of the  $\Psi$ -surface, the centre of gravity of the masses  $\mu$  and  $1-\mu$  placed at  $A$  and  $B$  represents through its three co-ordinates the composition, the volume, and the free energy of the complex which is obtained by simply placing  $\mu$  gram molecules of the phase  $A$  and  $1-\mu$  of the phase  $B$  next to each other without changing anything in the state of these phases. Every point of the join  $AB$  can thus represent a complex consisting of the phases  $A$  and  $B$ .

The second property concerns the question whether a phase or a complex of phases  $A$  will pass into another system whose  $\Psi$ -point  $B$  has the same horizontal projection as  $A$ . It is



evident that this is possible only if  $A$  lies above  $B$ . Just because the horizontal projections of  $A$  and  $B$  coincide, would the transformation take place without a change of volume, and under the assumed conditions the free energy of the system cannot increase.

A phase will thus be unable to split into two others if at the point which represents it all the sections are convex downward, in other words, if the surface lies entirely above the tangential plane.

The required conditions, which can again be deduced similarly as for the  $\zeta$ -surface (Art. 60), are

$$\frac{\partial^2 \Psi'}{\partial x^2} > 0, \quad \frac{\partial^2 \Psi'}{\partial v^2} > 0, \quad \frac{\partial^2 \Psi'}{\partial x^2} \frac{\partial^2 \Psi'}{\partial v^2} - \left( \frac{\partial^2 \Psi'}{\partial x \partial v} \right)^2 > 0, \quad . \quad (126)$$

of which the first or the second is again contained in the remaining two.

These conditions are certainly not satisfied between two inflexion points of a  $\Psi v$ -line or a  $\Psi x$ -line. Beyond the inflexion points, to the left of  $B$  and to the right of  $C$  (Fig. 22) there is a portion of the curve where the first two conditions are satisfied but not the third, since this requires that  $\frac{\partial^2 \Psi'}{\partial x^2} \frac{\partial^2 \Psi'}{\partial v^2}$  shall not only be positive but exceed a certain positive value. The points  $D$  and  $E$  at and beyond which the last condition is satisfied lie beyond the inflexion points. The points such as  $D$  and  $E$  of all the  $\Psi v$ -sections lie upon the so-called spinodal line which is determined by the equation

$$\frac{\partial^2 \Psi'}{\partial x^2} \frac{\partial^2 \Psi'}{\partial v^2} - \left( \frac{\partial^2 \Psi'}{\partial x \partial v} \right)^2 = 0. \quad . \quad . \quad . \quad (127)$$

96. We are now in the position to answer also the question concerning coexisting phases. *Two phases can be in equilibrium with each other if they are represented by the two contact points of a double tangential plane.*

This important property can be proved in two ways, geometrically and analytically. The geometrical proof has much in common with that for a  $\zeta$ -surface (Art. 63), and may be left to the reader.

The analytical proof is as follows :

As equilibrium conditions for two phases consisting of two components we have found (Art. 76)

$$\left(\frac{\partial \Psi}{\partial x}\right)_1 = \left(\frac{\partial \Psi}{\partial x}\right)_2 \quad . \quad . \quad . \quad . \quad (128)$$

$$\left(\frac{\partial \Psi}{\partial v}\right)_1 = \left(\frac{\partial \Psi}{\partial v}\right)_2 \quad . \quad . \quad . \quad . \quad (129)$$

$$\left(\Psi - x \frac{\partial \Psi}{\partial x} - v \frac{\partial \Psi}{\partial v}\right)_1 = \left(\Psi - x \frac{\partial \Psi}{\partial x} - v \frac{\partial \Psi}{\partial v}\right)_2 \quad . \quad (130)$$

The first two conditions express that the tangential planes at the two points representing the coexisting phases are parallel, and the third equation says that they cut off equal segments on the positive  $\Psi$ -axis. These tangential planes must therefore coincide with each other.

We thus find two coexisting phases determined by the points of contact of a double tangential plane. This, of course, is only possible if the surface has a plait. If this be a transversal plait the double tangential plane indicates a vapour phase coexisting with a liquid phase. By moving the double tangential plane over the plait to different positions we find each time two such coexisting phases. The locus of the points of contact of the double tangential planes is a curve which is termed the *connodal* line. The joins of pairs of these points of contact, i.e. the bitangents, lie upon a certain ruled surface. In Fig. 22,  $F$  and  $G$  may be taken to represent points of the connodal line. Notice that the values of  $x$  at the two points of contact of a double tangential plane are, in general, not equal, so that the points  $F$  and  $G$  of the connodal line which lie on the same  $\Psi v$ -section do not represent coexisting phases.

It may happen that the plait does not stretch over the whole  $\Psi$ -surface but ends in a point, at which, as it were, the two coexisting phases coincide. Such a point is termed a *plaitpoint*. If the critical temperature of the mixtures attains a maximum or a minimum, two such points may exist.

97. The mathematical theory of the plaitpoint has been worked out by Korteweg.\* We take from it what follows.

The plaitpoint,  $P$ , is a point of the connodal line at which the two contact points of the double tangential plane of the  $\Psi$ -surface coincide with each other. This point lies also on the

\* Archives néerlandaises, *T.* xxiv.

spinodal line. To show this, let us consider two coexisting phases *A* and *B* infinitely near the plaitpoint.

Let  $\delta v$  be the increment of volume and  $\delta x$  that of *x* in passing from *A* to *B*. In virtue of the equilibrium conditions  $\partial\Psi/\partial x$  as well as  $\partial\Psi/\partial v$  must have the same values at *A* and *B*. Consequently,

$$\frac{\partial^2\Psi}{\partial x^2}\delta x + \frac{\partial^2\Psi}{\partial x\partial v}\delta v = 0$$

and

$$\frac{\partial^2\Psi}{\partial x\partial v}\delta x + \frac{\partial^2\Psi}{\partial v^2}\delta v = 0,$$

whence

$$\frac{\partial^2\Psi}{\partial x^2\partial v^2} \frac{\partial^2\Psi}{\partial v^2} - \left(\frac{\partial^2\Psi}{\partial x\partial v}\right)^2 = 0,$$

which is the equation of the spinodal line. Thus, if the points *A* and *B* coincide with the plaitpoint, they will at the same time lie on the spinodal line.

98. In order to investigate the  $\Psi$ -surface in the neighbourhood of its plaitpoint *P*, we take this point as the origin of a rectangular system of co-ordinates, the tangential plane at *P* to the  $\Psi$ -surface as the *xy*-plane, and the tangent at *P*, which is the limit of the bitangents, as *y*-axis. This tangent has four coinciding points with the surface in common. In fact, the join of the points of contact *A* and *B* of a double tangential plane has at *A* as well as at *B* two coinciding points in common with the surface, so that at the plaitpoint two double points coincide.

Now, at a small distance from the origin, *z* can be developed into a series of ascending powers of *x* and *y*, where *x*, *y*, and *z* are the co-ordinates of a point of the  $\Psi$ -surface in the new system of axes. In general one would have

$$z = a + b_1x + b_2y + c_1x^2 + c_2xy + c_3y^2 \\ + d_1x^3 + d_2x^2y + d_3xy^2 + d_4y^3 + e_1x^4 + e_2x^3y + \dots$$

In the present case, however, a number of coefficients drop out. In the first place, *a*; then *b*<sub>1</sub> and *b*<sub>2</sub>, since  $\partial z/\partial x = 0$  and  $\partial z/\partial y = 0$  at *P*. Again,  $\partial^2 z/\partial y^2 = 0$  and  $\partial^3 z/\partial y^3 = 0$ , since the *y*-axis has at *P* four points in common with the surface. Thus also *c*<sub>3</sub> and *d*<sub>4</sub> must vanish. Finally, since the origin *P* lies upon the spinodal line,

$$\frac{\partial^2 z}{\partial x^2} \frac{\partial^2 z}{\partial y^2} - \left(\frac{\partial^2 z}{\partial x\partial y}\right)^2 = 0, \quad \dots \quad (131)$$

and we have also  $c_2=0$ . In fact, the left-hand member of the equation (127) found in Art. 95 for the spinodal line is invariant for all systems of rectangular co-ordinates, which justifies us in writing for this line the formula (131).

99. Thus, limiting ourselves to very small values of  $x$  and  $y$ , we can write

$$z = c_1x^2 + d_3xy^2 + e_5y^4$$

$$\text{or} \quad z = cx^2 + d \cdot xy^2 + ey^4. \quad . \quad . \quad . \quad (132)$$

We will assume that none of the coefficients  $c$ ,  $d$ ,  $e$  is nil. If one of them vanishes, special cases arise which will here be left out of account.

In explanation of (132) we may add that, since a term in  $x^2$  has survived, all higher powers of  $x$  as well as products of  $x^2$  into a power of  $y$  can be neglected in a first approximation. Similarly all terms differing from  $xy^2$  and  $y^4$  by powers of  $x$  or  $y$  can be omitted. The three terms in (132), however, must be retained, as they can very well be of the same order.

The coefficients  $c$ ,  $d$ ,  $e$  will depend upon the particular shape of the surface.

Now, the tangential plane at the plaitpoint may either intersect the surface or not. We limit ourselves to the latter case or to a plaitpoint of "the first kind". We thus assume that  $z$  vanishes only at the origin, *i.e.* that the equation

$$cx^2 + d \cdot xy^2 + ey^4 = 0$$

has no other roots than  $x=0$ ,  $y=0$ . The necessary condition is

$$4ce - d^2 > 0. \quad . \quad . \quad . \quad . \quad (133)$$

Again, without loss to generality,  $c$  can be made positive; this simply fixes the direction of the  $z$ -axis. By (133) the coefficient  $e$  will then be positive. Also  $d$  can be made positive by choosing properly the positive sense of the  $x$ -axis. To obtain an insight into the form of the surface we investigate its section by a plane parallel to the  $xy$ -plane for a very small value of  $z$ , a positive one, that is; for a negative value of  $z$  the section is imaginary.

The equations of this section (the so-called *indicatrix*) are

$$cx^2 + d \cdot xy^2 + ey^4 = z_0 \quad \text{and} \quad z = z_0.$$

The first of these, which determines the projection upon the  $xy$ -plane, can be written

$$x = -\frac{d}{2c}y^2 \pm \sqrt{\frac{z_0}{c} - \frac{4ce - d^2}{4c^2}y^4}. \quad (134)$$

The parabola

$$x = -\frac{d}{2c}y^2$$

forms a kind of axis of the curve (134), inasmuch as the points of the curve are found by laying off from each point of the parabola on both sides the same segment parallel to the  $x$ -axis.

For  $y=0$  this segment is equal to  $\sqrt{z_0/c}$ .

For increasing  $y$  this segment becomes smaller and vanishes for a certain value of  $y$ . This value of  $y$  is (Fig. 23)

$$OC = \left[ \frac{4cz_0}{4ce - d^2} \right]^{\frac{1}{4}}.$$

The figure is symmetrical with respect to the  $x$ -axis. We can now form an idea of the curve  $AKB$  [which is one-half of the projected section for a certain value of  $z_0$ ]. At the point  $K$  which has the ordinate  $y=OC$ , and which lies therefore on the said parabola, the tangent is parallel to the  $x$ -axis. The smaller  $z_0$ , the more slender the curve, while the parabola remains always the same;  $OC$  is proportional to  $z_0^{1/4}$ , whereas  $OA=OB$  is proportional to  $z_0^{1/2}$ . When  $z_0$  diminishes continually,  $OC$  becomes very large compared with  $OA$ , *i.e.* the curve becomes always longer in relation to its breadth. At the plaitpoint itself the  $\Psi$ -surface has no curvature in the direction of the  $y$ -axis, though it is curved along the  $x$ -axis, so that it resembles there somewhat a cylinder.

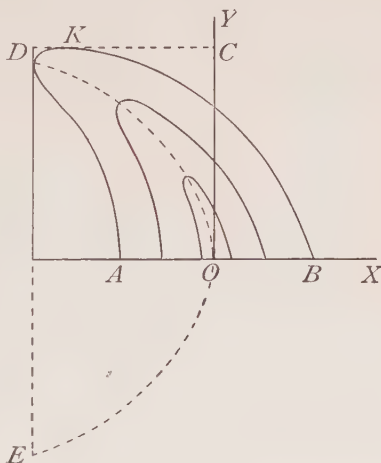


FIG. 23.

Particular attention deserves the point  $D$ , where the tangent is parallel to the  $y$ -axis. From formula (134) we have

$$\frac{\partial x}{\partial y} = -\frac{d}{c}y \mp \frac{(4ce - d^2)y^3}{2c^2 \sqrt{\frac{z_0}{c} - \frac{4ce - d^2}{4c^2}y^4}}.$$

(We write  $\partial x/\partial y$  to prevent a confusion with the coefficient  $d$ .)

Thus,  $\partial x/\partial y$  vanishes, for  $y=0$  and for  $y = \pm \left[ \frac{d^2 z_0}{e(4ce - d^2)} \right]^{\frac{1}{4}}$ . The first root does not tell us anything new. The second gives the ordinate  $y$  of the point  $D$  and of the point  $E$ , symmetrical to  $D$  with respect to the  $x$ -axis. Thus,

$$y_D = \left[ \frac{d^2 z_0}{e(4ce - d^2)} \right]^{\frac{1}{4}}. \quad (135)$$

This value of  $y$  is somewhat smaller than that for  $K$ , since  $4ce > d^2$ . For the abscissa of  $D$  we find

$$x_D = -2e \sqrt{\frac{z_0}{e(4ce - d^2)}}. \quad (136)$$

With diminishing  $z_0$  the ratio  $y_D : x_D$  continually increases, whence we see again that the section becomes the more slender the more we approach the tangential plane.

100. We will now show that  $DE$ , the double tangent of our curve, is the projection of a bitangent of the  $\Psi$ -surface, and that, therefore, the tangential planes at the points  $D'$  and  $E'$ , of which  $D$  and  $E$  are the projections, coincide with each other.

Consider two points situated symmetrically with respect to the  $x$ -axis, *i.e.* having the same  $x$  and  $z$  but opposite  $y$ 's. Now,

$$\left. \begin{aligned} \frac{\partial z}{\partial x} &= 2cx + dy^2 \\ \frac{\partial z}{\partial y} &= 2dxy + 4ey^3 \end{aligned} \right\}, \quad (137)$$

so that at these two points  $\partial z/\partial x$  has the same and  $\partial z/\partial y$  opposite values. But  $\partial z/\partial y$  is nil for the points  $D'$  and  $E'$ , as will be seen by substitution of  $x_D$  and  $y_D$ . Thus the tangential planes at  $D'$  and  $E'$  coincide with each other, which was to be proved.

Now, the connodal line is the locus of points such as  $D'$  and  $E'$ . Thus, to find the equation of the projection of this



line (the dotted line in Fig. 23), it is enough to eliminate  $z_0$  between (135) and (136). This gives

$$x = -\frac{2e}{d}y^2. \quad . \quad . \quad . \quad . \quad . \quad (138)$$

The equation of the spinodal line is, by Art. 95,

$$\frac{\partial^2 z}{\partial x^2} \frac{\partial^2 z}{\partial y^2} - \left( \frac{\partial^2 z}{\partial x \partial y} \right)^2 = 0,$$

where the values of the derivatives are determined by (137). This gives

$$x = -\frac{6ce - d^2}{cd}y^2, \quad . \quad . \quad . \quad . \quad . \quad (139)$$

which is again a parabola.

We have thus, successively, come across three parabolæ which touch each other at the origin  $O$  :

- I.  $x = -\frac{d}{2c}y^2$ , the axis (or mid-line) of the indicatrix.
- II.  $x = -\frac{2e}{d}y^2$ , the connodal line.
- III.  $x = -\frac{6ce - d^2}{cd}y^2$ , the spinodal line.

Now, 
$$\frac{6ce - d^2}{cd} > \frac{2e}{d} > \frac{d}{2c} > 0.$$

Thus the first parabola deviates from the  $y$ -axis less than the second, and the second less than the third. Cf. Fig. 24.

That these three curves are all parabolæ need not surprise us. This is merely due to the neglect of higher powers of  $x$  and  $y$  in developing  $z$ . Thus also do the results hold only in the neighbourhood of the plaitpoint.

101. The plaitpoint can also be deduced from the equation of the  $\Psi$ -surface itself. Of course, in doing so we must avail ourselves of a given form of the equation of state. We will keep to van der Waals' equation (81), as we have done hitherto.

Now, the equation of the spinodal line is

$$f \equiv \frac{\partial^2 \Psi}{\partial x^2} \frac{\partial^2 \Psi}{\partial v^2} - \left( \frac{\partial^2 \Psi}{\partial x \partial v} \right)^2 = 0, \quad . \quad . \quad . \quad (140)$$

and since the function  $f$  can be evaluated by means of formula (81), this gives already one condition for the co-ordinates of the

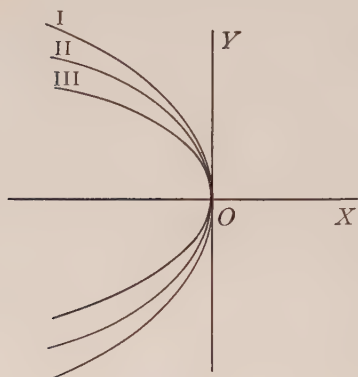


FIG. 24.

plaitpoint. The second condition is obtained by noticing that, if we move from the plaitpoint over an infinitesimal distance along the spinodal line, the pressure remains unaltered. To see this, it is enough to recall that in two coexisting phases and thus also at the two points of contact of a double tangential plane the pressure is the same. If now the curve  $BKDAE$  in Fig. 23 is allowed to contract, the points having  $D$  and  $E$  for

their projections pass into two infinitely near points of the connodal line, and thus also of the spinodal line,\* placed at  $O$ .

The variations of  $x$  and  $v$  due to a displacement along the spinodal line satisfy the condition

$$\frac{\partial f}{\partial x} \delta x + \frac{\partial f}{\partial v} \delta v = 0. \quad (141)$$

Now, if  $p = -\partial \Psi / \partial v$  is to remain unaltered by the displacement, we must have

$$\frac{\partial^2 \Psi}{\partial x \partial v} \delta x + \frac{\partial^2 \Psi}{\partial v^2} \delta v = 0,$$

and therefore, by (141),

$$\frac{\partial^2 \Psi}{\partial x \partial v} \frac{\partial f}{\partial v} - \frac{\partial^2 \Psi}{\partial v^2} \frac{\partial f}{\partial x} = 0.$$

Replacing here  $f$  by its value as given by (140), one finds

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x \partial v} \frac{\partial^2 \Psi}{\partial x^2} \frac{\partial^3 \Psi}{\partial v^3} - 3 \left( \frac{\partial^2 \Psi}{\partial x \partial v} \right)^2 \frac{\partial^3 \Psi}{\partial x \partial v^2} \\ + 3 \frac{\partial^2 \Psi}{\partial v^2} \frac{\partial^2 \Psi}{\partial x \partial v} \frac{\partial^3 \Psi}{\partial x^2 \partial v} - \left( \frac{\partial^2 \Psi}{\partial v^2} \right)^2 \frac{\partial^3 \Psi}{\partial x^3} = 0. \end{aligned} \quad (142)$$

Solving (140) and (142) for  $x$  and  $v$ , the co-ordinates of the plaitpoint could be determined. The calculation, however, is very complicated.

\* Since these two lines touch each other at  $O$ .

102. *Plaitpoint line*.—Let us imagine a family of  $\Psi$ -surfaces constructed for different values of temperature. Each of them will have its plaitpoint, and we can speak of a *plaitpoint line*, the locus of plaitpoints for different temperatures. The equation of the horizontal projection of this line will be found by eliminating  $T$  between (140) and (142). This is feasible, since, by (81),  $T$  occurs in  $\Psi$  itself in the first power and, therefore, in (140) in the second, and in (142) in the third power.

We have considered only the case in which the tangential plane at the plaitpoint does not cut the surface, referring to such a plaitpoint as one of the first kind (Art. 99).

The case  $4ce - d^2 < 0$ , in which that plane cuts the  $\Psi$ -surface (when we would have a plaitpoint of “the second kind”), will still be left alone. Likewise, the special cases which may arise when the coefficients  $c, d, e$  in (132) are given particular values.

103. *Variation of pressure due to an infinitesimal change of a state of equilibrium*.—To give one more example of the conclusions which can be obtained by means of the theory developed above, we will investigate how the pressure changes when, keeping the temperature constant, we pass from one state of equilibrium between a liquid and a gaseous phase to another, neighbouring state of equilibrium.

The tangential plane at any point  $P(x, v, \Psi)$  of the surface can be determined by the segments  $g$  and  $h$  which it cuts off on the  $\Psi$ -axis and on a line parallel to it drawn through the point of the fundamental plane having the co-ordinates  $x = 1, v = 0$ .

One finds without trouble

$$g = \Psi - x \frac{\partial \Psi}{\partial x} - v \frac{\partial \Psi}{\partial v} = \Psi - x \frac{\partial \Psi}{\partial x} + pv$$

and

$$h = g + \frac{\partial \Psi}{\partial x}.$$

The increments of  $g$  and  $h$  in passing from  $P$  to a neighbouring point are

$$dg = -x \frac{\partial^2 \Psi}{\partial x^2} dx - x \frac{\partial^2 \Psi}{\partial x \partial v} dv + v dp,$$

$$dh = (1-x) \frac{\partial^2 \Psi}{\partial x^2} dx + (1-x) \frac{\partial^2 \Psi}{\partial x \partial v} dv + v dp,$$

whence

$$(1-x)dg + xdh = vdp. \quad . \quad . \quad . \quad (143)$$

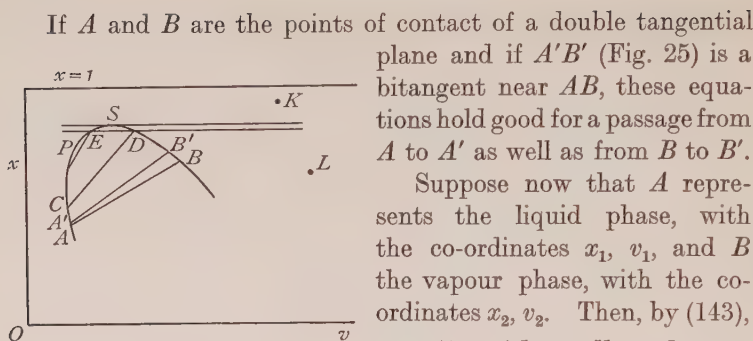


FIG. 25.

If  $A$  and  $B$  are the points of contact of a double tangential plane and if  $A'B'$  (Fig. 25) is a bitangent near  $AB$ , these equations hold good for a passage from  $A$  to  $A'$  as well as from  $B$  to  $B'$ .

Suppose now that  $A$  represents the liquid phase, with the co-ordinates  $x_1, v_1$ , and  $B$  the vapour phase, with the co-ordinates  $x_2, v_2$ . Then, by (143),

$$(1 - x_1)dg + x_1dh = v_1dp,$$

$$(1 - x_2)dg + x_2dh = v_2dp,$$

whence  $(v_2 - v_1)dp = (x_2 - x_1)d(h - g)$ . . . . . (144)

This equation has to be expanded in such a way as to exhibit the connection between  $dp$  and  $dx_1$  or  $dx_2$ . Now, from

$$h - g = \frac{\partial \Psi}{\partial x}$$

follows

$$d(h - g) = \frac{\partial^2 \Psi}{\partial x^2} dx + \frac{\partial^2 \Psi}{\partial x \partial v} dv. \quad . \quad . \quad . \quad (145)$$

To obtain what is to be substituted into (144), we have to take the right-hand member of (145) either for the passage from  $B$  to  $B'$  or for that from  $A$  to  $A'$ .

Further, instead of  $dv$  we have to introduce  $dp$ . Now,  $T$  being fixed once and for all,  $v$  can be considered as a function of  $x$  and  $p$ . Thus,

$$dv = \left( \frac{\partial v}{\partial x} \right)_p dx + \left( \frac{\partial v}{\partial p} \right)_x dp,$$

where we substitute

$$\left( \frac{\partial v}{\partial x} \right)_p = - \frac{(\partial p / \partial x)_r}{(\partial p / \partial v)_x} = - \frac{\partial^2 \Psi / \partial x \partial v}{\partial^2 \Psi / \partial v^2}$$

and

$$\left( \frac{\partial v}{\partial p} \right)_x = - \frac{(\partial v / \partial x)_p}{(\partial p / \partial x)_r} = \frac{(\partial v / \partial x)_p}{\partial^2 \Psi / \partial x \partial v}.$$

With the value of  $dv$  thus found equation (145) becomes

$$d(h - g) = \left\{ \frac{\partial^2 \Psi}{\partial x^2} - \frac{\left( \frac{\partial^2 \Psi}{\partial x \partial v} \right)^2}{\partial^2 \Psi / \partial v^2} \right\} dx + \left( \frac{\partial v}{\partial x} \right)_p dp.$$

Ultimately, substituting into (144) the values which this expression assumes for the passage from  $B$  to  $B'$  and for that from  $A$  to  $A'$ , we find the two equations

$$\left[ v_2 - v_1 - (x_2 - x_1) \left( \frac{\partial v_1}{\partial x_1} \right)_p \right] dp = (x_2 - x_1) \left\{ \frac{\frac{\partial^2 \Psi}{\partial x^2} \frac{\partial^2 \Psi}{\partial v^2} - \left( \frac{\partial^2 \Psi}{\partial x \partial v} \right)^2}{\partial^2 \Psi / \partial v^2} \right\}_1 dx_1 \quad (146)$$

$$\left[ v_2 - v_1 - (x_2 - x_1) \left( \frac{\partial v_2}{\partial x_2} \right)_p \right] dp = (x_2 - x_1) \left\{ \frac{\frac{\partial^2 \Psi}{\partial x^2} \frac{\partial^2 \Psi}{\partial v^2} - \left( \frac{\partial^2 \Psi}{\partial x \partial v} \right)^2}{\partial^2 \Psi / \partial v^2} \right\}_2 dx_2. \quad (147)$$

104. Let us examine these formulæ more closely. In equation (80) which expresses the relation between pressure and volume the only magnitudes depending on the composition  $x$  are  $a$  and  $b$ . Consequently, for the vapour phase, in which the molecular attraction and the finite dimensions of the molecules are of little importance, the derivative  $(\partial v_2 / \partial x_2)_p$  will differ but little from zero. (For, as is scarcely necessary to add, in our formulæ  $v$  is always the volume of a gram molecule of the mixture.)

The difference  $v_2 - v_1$  is not much smaller than  $v_2$ , the volume of the vapour phase, while  $x_2 - x_1$  is certainly smaller than 1. The coefficient of  $dp$  in the left-hand member of (147) is thus positive. The bracketed expression in the right-hand member is again positive, since we have to do with stable phases. Consequently, the sign of  $dp$  is the same as that of  $(x_2 - x_1)dx_2$ .

In equation (146) the derivative  $(\partial v_1 / \partial x_1)_p$  belonging to the liquid phase is of the same order as  $v_1$ , so that here the coefficient of  $dp$  is again positive and the sign of  $(x_2 - x_1)dx_1$  will agree with that of  $dp$ .

Consequently,  $dx_1$  and  $dx_2$  will have the same sign, which means that, when the composition of the liquid phase is changed, that of the vapour phase changes in the same sense.

It appears, further, that  $dp$  has the same sign as  $dx_1$  and  $dx_2$  if  $x_2 > x_1$ , and the opposite sign if  $x_1 > x_2$ . This can be expressed in words as follows. Let us call that component of which the vapour is relatively more abundant the volatile one. Then the vapour pressure is the greater the more of the volatile component the mixture contains.

While two phases in equilibrium with each other have in general different compositions, these can in a special case become equal. Suppose that  $x_1$  (which corresponds to the liquid phase) is allowed to increase steadily and that  $x_2$  is initially greater than  $x_1$ , then, when  $x_1$  attains a certain value,  $\bar{x}_1$  becomes equal to  $x_1$  and finally smaller than  $x_1$ . Then, by (146),  $p$  will first increase, reach its maximum for  $x_1 = \bar{x}_1$ , and then decrease. On the other hand, if first  $x_2 < x_1$  and then  $x_2 > x_1$ , the pressure for coinciding  $x_1$  and  $x_2$  will be a minimum.

The properties of the difference  $x_2 - x_1$  are exhibited in the graphical representation by the bitangent, *i.e.* the line joining the points of contact of the double tangential plane. For  $x_2 = x_1$ , the projection of the bitangent is parallel to the  $x$ -axis, and it deviates from the  $x$ -axis in opposite directions for  $x_2 > x_1$  and  $x_2 < x_1$ . If the double tangential plane is allowed to roll over the  $\Psi$ -surface, the direction of the projected bitangent will gradually change, tending to the direction of the  $v$ -axis when one of the edges ( $x=0$  or  $x=1$ ) of the  $\Psi$ -surface is approached—provided that the plait extends so far. In fact, we obtain as limiting case the equilibrium between two phases of one component only, so that  $x_1$  and  $x_2$  become both 0 or both 1. If the plait ends in a plaitpoint, the projection of the bitangent approaches the tangent of the projection of the connodal line, which tangent can deviate more or less from the direction of the  $v$ -axis.

105. *Lines of constant pressure.*—We may now explain in a few words how such lines could be found. Assuming any particular value  $\bar{p}$  for the pressure, we can seek upon each  $\Psi v$ -section of the  $\Psi$ -surface, *i.e.* upon each isothermal of a mixture of a given composition, the point at which the tangent has the direction determined by  $\partial\Psi/\partial v = -\bar{p}$ . The required line will be the locus of the points thus determined. If the temperature  $T$  lies above the critical temperature (Art. 92) of the mixture of chosen composition  $x$ , there is only one tangent of given direction. If, however,  $T$  lies below the critical temperature, then, according to the value of  $p$ , we have either one or three tangents.

The line  $p = \bar{p}$  can, of course, extend over parts of the surface which represent labile phases.



106. *Isothermal compression of a mixture.*—A point  $P$  of a bitangent, joining the points  $A$  and  $B$  of a double tangential plane, represents a complex of the phases  $A$  and  $B$ , the ratio of the quantities of  $A$  and  $B$  contained in the complex being given by the ratio of the distances  $BP$  and  $AP$  (Art. 95). The free energy of this complex, which is represented by the height of  $P$  above the horizontal plane, is smaller than the free energy of a homogeneous mixture of the same quantities of the two components.

By allowing the double tangential plane to roll over the  $\Psi$ -surface we obtain successively all the bitangents. These lie upon a ruled surface  $R$  which closes the plait from below and, together with the part of the  $\Psi$ -surface outside the connodal line, forms the “experimental”  $\Psi$ -surface, representing, that is, actually stable states, accessible to observation. There are still possible states represented by points between the connodal and the spinodal lines; these satisfy the stability conditions of Art. 95, so that a splitting into two phases of slightly different composition is here excluded. Also these points, however, lie above the ruled surface  $R$  (viz. above its edge), and each of the corresponding homogeneous phases will pass, under diminution of free energy, of course, into a complex of two phases represented by a point of  $R$  (cf. Art. 51). These “metastable” phases will therefore be left out of account. As regards the points of the  $\Psi$ -surface within the spinodal line, which lie above the middle part of the ruled surface  $R$ , the states represented by them cannot, on the whole, be realised since they are unstable even with respect to very small changes.

The projection of the experimental  $\Psi$ -surface upon the  $xv$ -plane consists of the projection of the  $\Psi$ -surface outside the connodal line and of the projection of the ruled surface within; in the latter part are contained the projections  $K$  of the bitangents which begin and end upon the projection  $C$  of the connodal line.

We can now readily see from the graphical representation what happens when a mixture which initially occupies a large volume, and thus is homogeneous, is compressed isothermally. It is enough to draw through the point of the horizontal plane which represents the initial state a line  $Q$  parallel to the  $v$ -axis. If this line does not cut the projection  $C$  just mentioned (as it

may happen, if the plait does not extend over the whole breadth of the surface and if the starting-point is so placed as  $K$  in Fig. 25), then the mixture will remain homogeneous. If, however, the line  $Q$  cuts  $C$  in two points  $D$  and  $E$ , then, as soon as through compression the volume  $v_D$  is reached, a splitting into two phases takes place which holds on until, at the volume  $v_E$ , the mixture becomes again homogeneous. Between  $D$  and  $E$  the quantities and the composition of the phases of the complex change continually in a manner indicated by the intersection of  $Q$  with the projections of the successive bitangents.

The boundary between these two cases (persistent homogeneity of the system and its splitting into two phases) is marked by the tangent to the projection of the connodal line drawn in the direction of the  $v$ -axis. A phase of a composition given by the ordinate  $x$  of the point of contact,  $S$  (Fig. 25), will just not split into two. This point  $S$  is called *the critical point of contact*.

It must still be mentioned that, if the point  $D$  where the line  $Q$  first cuts the projection  $C$  of the connodal line just happens to be the plaitpoint, the splitting into two phases takes place in a particular way. In fact, if this is not the case, the bitangent passing through  $D$  will cut the projection of the connodal line at a certain distance, and the next bitangent will then be cut by  $Q$  at a point which lies very near one of its end-points. The splitting begins then so that a small quantity of one phase is produced which differs considerably in composition from  $D$ , while the remaining substance assumes a state but slightly different from  $D$ . If, however,  $D$  is the plaitpoint, the first bitangent, which deviates infinitesimally from the direction of the tangent at the plaitpoint, will connect two points of the connodal line which lie at a small distance on both sides of the plaitpoint. The bitangent will now be cut by  $Q$  in a point which does not lie near one of its end-points. Thus two phases will be produced comparable with each other in quantity and both differing but slightly from the plaitpoint phase.

It is not difficult to see what will take place if the line  $Q$ , as can happen in Fig. 25, cuts the line  $C$  a second time, at the plaitpoint  $P$ .

107. *Retrograde condensation*.—A remarkable phenomenon takes place if the mixture which is being compressed has such a composition that the line  $Q$  of the preceding article falls between

the point of contact  $S$  and the point  $P$ . Suppose that the latter point, as in Fig. 25, lies on the side of smaller volumes, i.e. to the left from  $S$ , and let  $D$  be the first intersection point of the line  $Q$  with the projection of the connodal line. When in the process of compression this point is reached, liquid of a composition determined by the point  $C$  begins to appear. On further compression more liquid of continually varying composition is at first produced, but after a while (as can be seen from the figure) its quantity begins again to diminish until, on arriving at  $E$ , all the liquid will have vanished and we are left with a homogeneous vapour phase. This phenomenon, the *retrograde condensation*, was discovered by Kuenen in the case of mixtures of methylchloride and alcohol.

If the plaitpoint lies relatively to the critical point of contact on the side of greater volumes and if the line  $Q$  falls again between these two points, a phenomenon takes place which in a certain sense is the opposite of that just mentioned. A vapour phase is produced which on further compression ultimately disappears.

For a mixture of any given composition  $x$  a certain temperature may exist at which the critical point of contact lies on the line parallel to  $OV$  (with the given  $x$ ), and another temperature at which the plaitpoint lies on this line. The former is called the *critical mixing temperature*, and the latter the *plaitpoint temperature* of the mixture.

From what precedes it is evident that the critical phenomena in a mixture will differ entirely from those in a simple substance. For further details the reader may be referred to the second part of van der Waals' *Continuität des gasförmigen und flüssigen Zustandes*.



ENTROPY AND PROBABILITY  
(1910–1911)





## INTRODUCTION

1. ORIGINALLY, entropy (as well as free energy and the thermodynamical potential) was introduced into thermodynamics as a rather limited concept, namely, as a concept which was applicable only to states of equilibrium. Later the entropy concept was broadened, though at first in a more or less haphazard and groping way. Eventually, however, these extensions have assumed, mainly in connection with probability considerations, a more solid shape.

The original definition of entropy is

$$\eta = \int \frac{dQ}{T},$$

the integral to be taken along a reversible path. But just therein lies a great limitation. For all states along the integration path, including its limits, have to be states of equilibrium, so that the definition holds for such states only.

This limitation is sometimes very doubtful, since states of equilibrium, so far as entropy is concerned, are characterised by  $\eta = \text{maximum}$ . Now, to apply this criterion, one must be able to compare them with non-statical states, whereas, rigorously, according to the above, classical, thermodynamical definition, one cannot speak of the entropy of such states.

For the practical application to some cases this difficulty can be readily overcome. For example, in the case of a system of two phases not in equilibrium with each other we can imagine a wall separating the two phases and consider the entropy of either phase separately (since they are not in equilibrium only while they are in contact with each other). In other cases, however, the matter is not so simple. Such, for instance, is the

case of *dissociation*.\* But we will leave these considerations on one side and turn to the proper subject of our lectures.

\* As a matter of fact, Prof. Lorentz treated here the problem of dissociation equilibrium, but since such investigations were embodied by Mrs. T. C. Clay-Jolles into the course of lectures on Thermodynamics (E. J. Brill, Leiden, 1921), they can here be appropriately omitted. C. [Cf. p. 116 of this volume.]

## CHAPTER I

### BOLTZMANN'S PROBABILITY METHOD

#### 2. MAXWELL'S LAW DERIVED BY BOLTZMANN'S METHOD

WE will begin with Boltzmann's deduction of Maxwell's distribution law of velocities based on probability considerations.

Let us consider a monatomic gas and, to express its state in an auxiliary graph (the "velocity diagram"), let us represent the velocity of each molecule by a vector  $OP$  drawn from a fixed point  $O$ . The end-point  $P$  of the vector will be the "velocity point" of the molecule. Let  $dS$  be any volume element of the velocity diagram. Then, speaking statistically, the state of the gas will be completely known if the number of molecules in each  $dS$  be given.

We assume that the velocity diagram is of finite extent and we divide it into a (finite) number  $k$  of equal elements  $dS_1, \dots, dS_k$ , with a view of passing in our final results to the limit for  $k = \infty$ . Let there be in all  $n$  molecules whose velocity points are distributed among the elements  $dS_1, \dots, dS_k$ , and let us determine the distribution of these points by drawing lots. We arrange this lottery as follows: We take an urn with  $k$  balls, marked 1 up to  $k$ , a ball for each element  $dS$ . We draw once for each molecule and replace each time the ball drawn in the urn. This ensures to each molecule exactly the same chance as to which element is to be allotted to it.

By repeating such a lottery many times one could determine the frequency of all possible distributions and thus find out experimentally which of them is the most probable one.

To begin with, we ask what is the probability of obtaining by

means of the described lottery a *determined distribution*, a distribution, that is, in which

$$\begin{array}{ccccccc} n_1 & \text{determined} & \text{molecules} & \text{lie in} & dS_1, \\ n_2 & & & & dS_2, \\ . & . & . & . & . \\ n_k & & & & dS_k. \end{array}$$

This probability is

$$w = \left(\frac{1}{k}\right)^n, \quad (1a)$$

for, each time we draw for a molecule, the probability of its falling just into that element in which we desire to have it is  $1/k$ .

We now reduce somewhat our requirements and seek the probability that

$$\begin{array}{ccccccc} n_1 & \text{determined} & \text{molecules} & \text{fall into} & dS_1, \\ . & . & . & . & . \\ n_{k-2} & & & & dS_{k-2}, \\ \text{but } n_{k-1} & \text{arbitrary} & & & dS_{k-1}. \end{array}$$

To find this probability we have to multiply (1a) by the number of ways in which a group of  $n_{k-1}$  molecules can be chosen from the remaining  $n_{k-1} + n_k = n - n_1 - n_2 - \dots - n_{k-2}$  molecules. This number is

$$\frac{(n_{k-1} + n_k)!}{n_{k-1}! n_k!};$$

hence the required probability,

$$w = \frac{(n_{k-1} + n_k)!}{n_{k-1}! n_k!} \left(\frac{1}{k}\right)^n. \quad (1b)$$

In the next place we abolish the requirement of determinate molecules for  $dS_{k-2}$  also. The molecules for  $dS_1, \dots, dS_{k-3}$  being chosen,  $n_{k-2} + n_{k-1} + n_k$  molecules are left over. From these a group of  $n_{k-2}$  molecules can be chosen in

$$\frac{(n_{k-2} + n_{k-1} + n_k)!}{n_{k-2}! (n_{k-1} + n_k)!}$$

ways, and the probability for this case will be the product of this factor into (1b). In this manner we can proceed, abolishing each time the requirement of *determinate* molecules for a new element  $dS$  and thus introducing into the expression for the probability a new factor. The last of these factors will, evidently, be equal to



that it will certainly not correspond to reality. There is thus manifestly some error, or rather incompleteness, in our reasoning. This consists in not taking account of one more condition, viz. *that the total energy of all molecules shall have a completely determined value.*

Let  $\epsilon_1$  be the kinetic energy of a molecule when it lies in  $dS_1$ ; similarly,  $\epsilon_2$  when it lies in  $dS_2$ , and so on ( $\epsilon_i$  to be constant for each element  $dS_i$ ). Then our condition will be

$$n_1\epsilon_1 + n_2\epsilon_2 + \dots + n_k\epsilon_k = \epsilon = \text{total kinetic energy of the gas.} \quad (2)$$

In view of this condition the arrangement of the lottery must now be somewhat modified. We proceed as follows. We determine, as before, by drawing balls, a system of values of  $n_1, \dots, n_k$  and we verify whether it agrees with (2). In general this will not be the case, and the result will then be rejected. Only those results will count which satisfy (2).

Suppose now, we had found in this way two systems of values of the  $n$ 's satisfying (2),

$$n_1, n_2, \dots, n_k \text{ and } \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_k.$$

Then the probabilities of these two systems will be to each other as the corresponding values of  $w$ , i.e. as

$$\frac{n!}{n_1! n_2! \dots n_k!} \text{ to } \frac{n!}{\mathbf{n}_1! \mathbf{n}_2! \dots \mathbf{n}_k!}.$$

What is now the probability of either system?

Let the sum

$$\Sigma \frac{n!}{n_1! n_2! \dots n_k!} = A \quad \dots \quad (3)$$

be extended over all admissible systems of  $n$ 's, i.e. all those agreeing with (2). Then the probability of a given system will be

$$w = \frac{1}{A} \frac{n!}{n_1! n_2! \dots n_k!} \quad \dots \quad (4)$$

Notice in passing that for wholly arbitrary values of  $n_1, \dots, n_k$  (i.e. without taking account of the condition (2)) we have, as in (1e),

$$\Sigma \frac{n!}{n_1! n_2! \dots n_k!} = k^n,$$

and therefore,  $A < k^n$ , since the sum for  $A$  extends only over certain systems of values of  $n_1, \dots, n_k$ , namely, those only which satisfy (2). Again,  $A$  will depend on  $\epsilon$ , since for different values



of the energy the sum is to be extended over different systems  $n_1, \dots, n_k$ . But the question of the most probable distribution for a given  $\epsilon$  has nothing to do with this dependence.

To answer this question we have to look for a maximum of the expression (4) or, since  $A$  and  $n!$  are constant, for a minimum of the denominator or also of its logarithm. For this purpose we make use of Stirling's formula for the factorials of great numbers. For  $n_1!$  this formula is

$$n_1! = n_1^{n_1 + \frac{1}{2}} e^{-n_1} \sqrt{2\pi}.$$

Thus,

$$\log(n_1!) = (n_1 + \frac{1}{2}) \log n_1 - n_1 + \frac{1}{2} \log 2\pi,$$

$$\log(n_1! n_2! \dots n_k!) = (n_1 + \frac{1}{2}) \log n_1 + (n_2 + \frac{1}{2}) \log n_2 + \dots$$

$$+ (n_k + \frac{1}{2}) \log n_k - n + \frac{1}{2} k \log 2\pi.$$

The term  $\frac{1}{2}$  can be neglected in presence of  $n_1, \dots, n_k$ , and  $n$  as well as  $\frac{1}{2} k \log 2\pi$  are constants. Thus, what ultimately has to be made a minimum is

$$H = n_1 \log n_1 + n_2 \log n_2 + \dots + n_k \log n_k = \sum_1^k n \log n. \quad (5)$$

Let  $n_{01}, \dots, n_{0k}$  be the values of  $n_1, \dots, n_k$  for which  $H$  attains a minimum. Then it will still be very improbable that in a drawing of lots these values should come out *exactly*; but the deviations will be of the order of  $\sqrt{n_{01}}, \dots, \sqrt{n_{0k}}$ , and, therefore, quite small in comparison with the numbers  $n_{01}, \dots, n_{0k}$  themselves which are supposed to be large numbers.

Thus, when Boltzmann says that the most probable state corresponding to the values  $n_{01}, \dots, n_{0k}$  will actually ensue, he takes it for granted that deviations of the said order from these values may well occur.

Turning at last to the solution of our minimum problem, we have to find the conditions which must be satisfied by  $n_1, \dots, n_k$  in order that (5) shall be a minimum and that the conditions (1) and (2) shall be fulfilled.

Subjecting  $n_1, \dots, n_k$  to variations we have, by (1),

$$\delta n_1 + \delta n_2 + \dots + \delta n_k = 0, \quad (6)$$

further, by (2),

$$\epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \dots + \epsilon_k \delta n_k = 0, \quad (7)$$

and by (5),

$$\delta H = (1 + \log n_1) \delta n_1 + (1 + \log n_2) \delta n_2 + \dots + (1 + \log n_k) \delta n_k = 0. \quad (8)$$

We multiply \* (6) by  $C$ , (7) by  $C'$ , add the equations thus obtained to (8) and equate to zero the coefficients of  $\delta n_1, \dots \delta n_k$ . In this way we find for every term  $[\lambda = 1, 2, \dots k]$

$$1 + \log n_\lambda + C + C' \epsilon_\lambda = 0.$$

Put

$$-(1 + C) = \log a \text{ and } C' = l.$$

Then,

$$\log n_\lambda = \log a - l \epsilon_\lambda$$

or

$$n_\lambda = a e^{-l \epsilon_\lambda}.$$

This equation expresses Maxwell's distribution law. If  $\xi, \eta, \zeta$  be the velocity components and  $m$  the mass of a molecule, the equation becomes

$$n_\lambda = a e^{-\frac{1}{2} l m (\xi^2 + \eta^2 + \zeta^2)}.$$

The values of  $a$  and  $l$  (positive) are to be determined from the conditions (1) and (2).

### 3. EXTENSION OF BOLTZMANN'S TREATMENT

The above treatment is originally due to Boltzmann, but the form in which it has been here reproduced differs somewhat from that given by Boltzmann. It can be extended in various directions, as *e.g.* to diatomic molecules, to molecules which are subjected to external forces, and so on. Then, however, more magnitudes are needed for the determination of the state, and general co-ordinates will be appropriately introduced. Thus, let the position and the state of motion of a gas molecule be determined by the general co-ordinates  $q_1, \dots q_s$  and the momenta  $p_1, \dots p_s$ . Instead of being represented by a point of the three-dimensional velocity diagram with the velocity components  $\xi, \eta, \zeta$  as co-ordinates, the state of each molecule will now be represented by a point of a  $2s$ -dimensional diagram [space] with the  $q$ 's and the  $p$ 's as co-ordinates. As before, let this space be divided into  $k$  equal elements  $dS_1, \dots dS_k$  (to begin with,  $k$  is supposed to be finite).

The problem in each given case is then again reduced to the question of the distribution of the molecules over the elements.

Its solution will, *mutatis mutandis*, depend on exactly the same considerations as above. We have again the two conditions

$$n_1 + n_2 + \dots + n_k = n \text{ and } n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_k \epsilon_k = \epsilon.$$

---

\* [For a justification of this well-known procedure, cf. *Thermodynamics*, p. 60, *supra*.]

Possible interactions between the molecules which might contribute to the energy will be left out of account.

The lottery remains exactly the same as in the preceding simple case. Likewise, our considerations concerning the magnitude  $H$ . One finds again

$$n_\lambda = ae^{-\epsilon_\lambda}.$$

Since the elements  $dS_\lambda$  are supposed to be equal, this can also be written

$$n_\lambda = Ce^{-\epsilon_\lambda} dS_\lambda, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where  $C$  is some constant. This formula will still hold good when the elements are not of equal size. For it is readily seen that equal elements placed next each other contain equal numbers of molecules, so that at a given place  $n_\lambda$  must be proportional to  $dS_\lambda$ . The factor  $Ce^{-\epsilon_\lambda}$  can be looked upon as a density. By way of further explanation we may add that it is, of course, our intention to measure the elements in a determined way. The most obvious way is to assign to an element which contains molecules whose co-ordinates range from  $q_1$  to  $q_1 + dq_1$ , from  $q_2$  to  $q_2 + dq_2$ , etc., and whose momenta lie between  $p_1$  and  $p_1 + dp_1$ ,  $p_2$  and  $p_2 + dp_2$ , etc., the size  $dq_1 \dots dq_s \, dp_1 \dots dp_s$ . The underlying assumption is that, when the elements are *thus* measured, the distribution of the molecules over equal elements can be determined by the aforesaid lottery. Let us still notice that the element just defined by the extreme values  $q_1$  and  $q_1 + dq_1$ ,  $\dots$   $p_s$  and  $p_s + dp_s$  is a "2s-dimensional parallelepipedon." Now, this is an arbitrary choice. The elements may have another shape. But then we can divide them always into much smaller 2s-dimensional parallelepipeda and thus measure their sizes.

In fine, we can always write

$$\text{number of molecules in } dS = Ce^{-\epsilon} dS, \quad . \quad . \quad (10)$$

where  $\epsilon$  is the energy of a molecule in  $dS$ .

That, in order to obtain suitable results, the  $q$ 's and the  $p$ 's (co-ordinates and momenta), and not, for instance, the  $q$ 's and the  $\dot{q}$ 's (co-ordinates and velocities), have to be chosen as independent variables, can be made plain by the following reasoning.

For given molecules the co-ordinates  $q_1, \dots, q_s$  and the corresponding momenta  $p_1, \dots, p_s$  can be chosen in different

ways and the results, of course, which will thus be obtained must not clash with each other. The state of the gas cannot depend on the co-ordinates which it pleases us to introduce.

In formula (10),  $dS$  is the size of a volume-element expressed in what may be called the  $q, p$ -measure, *i.e.* that measure in which the size of a parallelepipedon is given by  $dq_1 \dots dp_s$ . If new co-ordinates  $q'_1, \dots, q'_s$  and the corresponding momenta are introduced, the size of *the same* volume-element can also be expressed in the  $q', p'$  measure. Now, if the new size be denoted by  $dS'$ , we have always

$$dS = dS',$$

and this beautiful property holds, in general, only when  $q_1, \dots, p_s$  and *not* other magnitudes, as *e.g.*  $q_1, \dots, \dot{q}_s$ , are chosen as independent variables. Since also the energy  $\epsilon$  is independent of the choice of co-ordinates, the result expressed by (10) will remain the same, no matter what co-ordinates are chosen.

*Proof of the last equality.*

By a theorem of many-dimensional geometry,

$$dS = \begin{vmatrix} \frac{\partial q_1}{\partial q'_1} & \dots & \frac{\partial p_s}{\partial q'_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial q_1}{\partial p'_s} & \dots & \frac{\partial p_s}{\partial p'_s} \end{vmatrix} dS', \quad \dots \quad (11)$$

so that we have only to prove that the determinant is equal to 1. Now, if the kinetic energy  $T$  is considered as a function of the co-ordinates and the velocities, we have

$$p_1 = \frac{\partial T}{\partial \dot{q}_1}, \dots, p_s = \frac{\partial T}{\partial \dot{q}_s}. \quad \dots \quad (12)$$

Again, since the new co-ordinates  $q'_1, \dots, q'_s$  depend only on  $q_1, \dots, q_s$  and not on  $p_1, \dots, p_s$ ,

$$\begin{aligned} \dot{q}'_1 &= \frac{\partial q'_1}{\partial q_1} \dot{q}_1 + \dots + \frac{\partial q'_1}{\partial q_s} \dot{q}_s \\ &\vdots \\ \dot{q}'_s &= \frac{\partial q'_s}{\partial q_1} \dot{q}_1 + \dots + \frac{\partial q'_s}{\partial q_s} \dot{q}_s \end{aligned} \quad \dots \quad (13)$$

As regards the momenta, it is most convenient to express the old values  $p_1, \dots, p_s$  in terms of the new ones,  $p'_1, \dots, p'_s$ .



The components of momentum corresponding to  $x, y, z$  are

$$m\dot{x}, m\dot{y}, m\dot{z}.$$

Let these co-ordinates be contained between  $x$  and  $x+dx$ , etc., and the components of momentum between  $m\dot{x}$  and  $m(\dot{x}+d\dot{x})$ , etc. Then, if  $d\lambda$  be the product of the differentials of the remaining co-ordinates and momenta,

$$dS = dx dy dz m^3 d\dot{x} d\dot{y} d\dot{z} d\lambda.$$

Let there be an external force which we may suppose to be applied at the centre of gravity and to depend upon the position of this point. Then, if  $\psi$  be the corresponding potential energy per unit mass, the total energy of a molecule will be

$$\epsilon = m\psi + \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \bar{\epsilon}, \quad (15)$$

where  $\bar{\epsilon}$  represents all other kinds of energy the molecule may possess in addition to those enumerated (such as energy of rotation, etc.);  $\epsilon$ , however, will be independent of  $x, y, z, \dot{x}, \dot{y}, \dot{z}$ .

Thus the number of molecules in  $dS$  will be

$$Ce^{-lm\psi + \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \bar{\epsilon}} m^3 dx \dots d\dot{z} d\lambda.$$

To find the number of molecules contained in a volume-element  $dx dy dz$  of the gas, this expression has to be integrated over all variables other than  $x, y, z$ . Since  $lm\psi$  is kept constant, the integral will become

$$Ce^{-lm\psi} dx dy dz m^3 \int e^{-l\{\frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \bar{\epsilon}\}} d\dot{x} d\dot{y} d\dot{z} d\lambda.$$

This number and, therefore, also the density of the gas is proportional to  $e^{-lm\psi}$ . We have thus found the known *barometric height formula*.

The mean kinetic energy of the translational motion of a molecule will now be found by evaluating

$$\bar{\dot{x}^2} = \frac{Ce^{-lm\psi} dx dy dz m^3 \int \dot{x}^2 e^{-l\{\frac{1}{2}m(\dot{x}^2 + \dots) + \bar{\epsilon}\}} d\dot{x} \dots d\lambda}{Ce^{-lm\psi} dx dy dz m^3 \int e^{-l\{\frac{1}{2}m(\dot{x}^2 + \dots) + \bar{\epsilon}\}} d\dot{x} \dots d\lambda}$$

and two similar expressions. Now, since both integrals contain the factor  $\int e^{-l\epsilon} d\lambda$ ,

$$\bar{\dot{x}^2} = \frac{\int_{-\infty}^{+\infty} \dot{x}^2 e^{-\frac{1}{2}lm\dot{x}^2} d\dot{x}}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2}lm\dot{x}^2} d\dot{x}} = \frac{1}{lm}. \quad (15a)$$



Consequently,

$$\bar{T} = \frac{1}{2}m(\bar{\dot{x}}^2 + \bar{\dot{y}}^2 + \bar{\dot{z}}^2) = \frac{1}{2}m \cdot \frac{3}{\bar{m}} = \frac{3}{2\bar{l}}.$$

The mean kinetic energy of a gas in thermal equilibrium is thus independent of  $x$ ,  $y$ ,  $z$ , or everywhere the same—a known result due to Maxwell. (The constant  $l$  is inversely proportional to the absolute temperature.)

#### 4. SOME APPLICATIONS OF BOLTZMANN'S METHOD

##### *a. Rotating gas.*

Let us consider a monatomic gas enclosed in a sphere whose inner surface is perfectly smooth. In addition to the usual heat motion the gas may be endowed with a variety of other motions. We will consider the case in which *the gas as a whole rotates around an axis* [passing through the centre of the sphere]. This will be our  $X$ -axis.

The containing vessel is supposed to be at rest, which makes no difficulty, since its inner wall is assumed to be perfectly smooth.

Let us consider the moment of momentum with respect to the centre.

The co-ordinates of a molecule being  $x$ ,  $y$ ,  $z$ , and its velocity components  $\xi$ ,  $\eta$ ,  $\zeta$ , the moment of momentum of the molecule with respect to the  $X$ -axis is

$$m(y\zeta - z\eta) = \chi,$$

and that of all molecules

$$\Sigma m(y\zeta - z\eta) = X.$$

If the gas is left to itself,  $X$  will evidently be a constant, regardless of the collisions of the molecules. Thus, in addition to the energy also  $X$  will now have a prescribed value.

The most probable state can again be determined by means of a lottery. We consider a six-dimensional diagram or space :  $x$ ,  $y$ ,  $z$ ,  $\xi$ ,  $\eta$ ,  $\zeta$ .

The conditions now are that the total number  $n$  of molecules, the total energy  $\epsilon$  and moment of momentum  $X$  shall have prescribed values.

In order to determine, for the most probable state, the

numbers of molecules  $n_1, \dots, n_k$  in the equal elements  $dS_1, \dots, dS_k$ , we have, exactly as before, to find the minimum of

$$H = n_1 \log n_1 + n_2 \log n_2 + \dots + n_k \log n_k,$$

subject in the present case to the three conditions

$$1^0 \quad n_1 + n_2 + \dots + n_k = n,$$

$$2^0 \quad n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_k \epsilon_k = \epsilon,^*$$

and

$$3^0 \quad n_1 \chi_1 + n_2 \chi_2 + \dots + n_k \chi_k = X.$$

The method of solving this problem is as before. (Cf. (6), (7), and (8).) Thus,

$$\delta n_1 + \delta n_2 + \dots + \delta n_k = 0, \quad . \quad . \quad . \quad (17)$$

$$\epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \dots + \epsilon_k \delta n_k = 0, \quad . \quad . \quad . \quad (18)$$

$$\chi_1 \delta n_1 + \chi_2 \delta n_2 + \dots + \chi_k \delta n_k = 0, \quad . \quad . \quad . \quad (19)$$

$$\delta H = (1 + \log n_1) \delta n_1 + (1 + \log n_2) \delta n_2 + \dots$$

$$+ (1 + \log n_k) \delta n_k = 0. \quad (20)$$

We multiply (18) by the constant  $l$ , (19) by  $\mu$ , and (17) by a third constant, add the resulting equations to (20) and equate to zero the coefficients of  $\delta n_1, \dots, \delta n_k$ . Thus the result assumes the form

$$\log n_\lambda = \log C - l\epsilon_\lambda - \mu\chi_\lambda$$

or

$$n_\lambda = Ce^{-l\epsilon_\lambda - \mu\chi_\lambda}.$$

This is the solution of the problem ( $C$ ,  $l$ , and  $\mu$  are determined by the three conditions).

Let us examine this result somewhat more closely. The number of molecules within the element  $dx dy dz d\xi d\eta d\zeta$  will be

$$Ce^{-l\epsilon - \mu\chi} dx \dots d\zeta = Ce^{-\frac{1}{2}lm(\xi^2 + \eta^2 + \zeta^2) - \mu m(y\xi - z\eta)} dx \dots d\zeta$$

$$= Ce^{-\frac{1}{2}lm\left[\xi^2 + \left(\eta - \frac{\mu}{l}z\right)^2 + \left(\zeta + \frac{\mu}{l}y\right)^2\right] + \frac{1}{2}m\frac{\mu^2}{l}(y^2 + z^2)} dx \dots d\zeta,$$

or, with the abbreviations

$$\eta - \frac{\mu}{l}z = \eta' \quad \text{and} \quad \zeta + \frac{\mu}{l}y = \zeta',$$

$$Ce^{-\frac{1}{2}lm(\xi^2 + \eta'^2 + \zeta'^2) + \frac{1}{2}m\frac{\mu^2}{l}(y^2 + z^2)} dx \dots d\zeta.$$

To determine the number of molecules contained in the volume-element  $dx dy dz$  of the gas, this expression has to be integrated over the velocity components, or also over  $d\xi, d\eta', d\zeta'$ ,

\* The energy  $\epsilon$  introduced before (cf. (15)) is left out, since there are no external forces and the gas is monatomic.

keeping  $y$  and  $z$  constant. The expression to be thus found will contain the factor

$$e^{\frac{1}{2}m\frac{\mu^2}{l^2}(y^2+z^2)},$$

to which, therefore, the density will be proportional. The density of the gas will thus vary with the distance from the  $X$ -axis (which can be ascribed to the centrifugal force).

In the next place we may consider the mean values of  $\xi$ ,  $\eta$ ,  $\zeta$  in a given volume-element. We find

$$\bar{\xi} = 0, \quad \bar{\eta}' = 0, \quad \bar{\zeta}' = 0,$$

whence

$$\bar{\eta} = \bar{\eta}' + \frac{\mu}{l}z = +\frac{\mu}{l}z,$$

$$\bar{\zeta} = \bar{\zeta}' - \frac{\mu}{l}y = -\frac{\mu}{l}y.$$

There is thus in the volume-element a certain mean velocity or velocity of streaming, and this is just the velocity which corresponds to an angular velocity  $-\mu/l$  about the  $X$ -axis.

The mean kinetic energy is

$$\begin{aligned} \bar{T} &= \frac{1}{2}m(\bar{\xi}^2 + \bar{\eta}^2 + \bar{\zeta}^2) = \frac{1}{2}m\left[\bar{\xi}^2 + \bar{\eta}'^2 + \bar{\zeta}'^2 + \frac{\mu^2}{l^2}(y^2 + z^2)\right] \\ &= \frac{3}{2}l + \frac{1}{2}m(y^2 + z^2)\frac{\mu^2}{l^2}; \end{aligned}$$

cf. (15a). It consists of two parts, the energy of heat agitation and that of rotation.

If the gas were at rest, the  $\chi$ -condition would also have to be taken into account, but then we would find that  $\mu$  must vanish.

#### *b. Equilibrium of two gases.*

In the next place we consider two monatomic gases separated by a thin metallic wall (so that the passage of heat is possible). This wall will be supposed to be so thin that its energy compared with that of the two gases can be neglected.

The first gas consists of  $n$ , and the second of  $n'$  molecules, the volume-elements in the velocity diagram of the first gas are  $dS_1, \dots, dS_k$ , and those in the velocity diagram of the second gas  $dS'_1, \dots, dS'_k$ , while the total energy of both gases has the given value  $\epsilon$ . This energy can be divided into two parts in a variety of ways; thus, *e.g.*, we can put

$$\epsilon = \epsilon + \epsilon',$$

where  $\epsilon$  is the energy of the first, and  $\epsilon'$  that of the second gas.

The most probable distribution of velocities can now be found by means of a lottery as was already done in the case of a single gas (taking account of the energy condition). We can try to find the most probable state by first arranging a lottery for each gas separately, as before, with fixed values of  $\epsilon$  and  $\epsilon'$ .

Let  $w$  be the probability that such a lottery gives for the first gas the distribution :

$$n_1 \text{ molecules in } dS_1,$$

$$n_2 \quad , , \quad dS_2,$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot$$

$$n_k \quad , , \quad dS_k,$$

and the energy  $\epsilon$ , and let  $w'$  be the probability of an analogous result for the second gas.

We could then seek, by the previous method, those distributions for which the probabilities  $w$  and  $w'$ , taken separately, attain their maximum values, with the assumed subdivision of the energy into two parts. But the question, what will be the actual distribution (and this is the point at issue), cannot very well be answered in this way. We prefer, therefore, to arrange a lottery for the whole system consisting of the two gases.

In doing so we will generalise the problem, viz. by extending it to polyatomic substances.

We introduce general co-ordinates and momenta, and distinguish for the molecules of the first gas the equal volume-elements  $dS_1, \dots, dS_k$  of the  $q, p$ -space, and similarly the equal volume-elements  $dS'_1, \dots, dS'_k$  for the second gas. The urn is supposed to contain  $k + k'$  marked balls, viz. two groups of balls, one corresponding to the former and the other to the latter volume-elements. Let now an "experiment" be considered as completed when by successively drawing balls it is determined for each of the  $n + n'$  molecules in which volume-element it is to be placed, it being understood that a drawing is valid for a molecule of the first gas only if a ball of the first group appears, and similarly for the molecules of the second gas.

We will suppose that many such experiments have been made and that ultimately only those are retained which yield for the total energy of the two gases the value  $\epsilon$ .

The required probability of  $n_1 \dots n_k, n'_1 \dots n'_k$  molecules being placed in the said elements is proportional to

$$\frac{(n+n')!}{n_1! \dots n_k! n'_1! \dots n'_k!}.$$

There is still a factor missing, but this is the same for all the experiments, so that for their comparison this expression only will be needed. The condition for its maximum is that

$H = n_1 \log n_1 + \dots + n_k \log n_k + n'_1 \log n'_1 + \dots + n'_k \log n'_k$  shall be a minimum. The supplementary conditions are

$$\begin{aligned} n_1 + \dots + n_k &= n \\ n'_1 + \dots + n'_k &= n' \\ n_1 \epsilon_1 + \dots + n_k \epsilon_k + n'_1 \epsilon'_1 + \dots + n'_k \epsilon'_k &= \epsilon. \end{aligned}$$

We subject these expressions to variations. From  $\delta H = 0$  we find

$$(1 + \log n_1) \delta n_1 + \dots + (1 + \log n_k) \delta n_k + (1 + \log n'_1) \delta n'_1 + \dots + (1 + \log n'_k) \delta n'_k = 0. \quad (23)$$

$$\text{Again,} \quad \delta n_1 + \dots + \delta n_k = 0 \quad . \quad . \quad . \quad (24)$$

$$\delta n'_1 + \dots + \delta n'_k = 0 \quad . \quad . \quad . \quad (25)$$

$$\epsilon_1 \delta n_1 + \dots + \epsilon_k \delta n_k + \epsilon'_1 \delta n'_1 + \dots + \epsilon'_k \delta n'_k = 0 \quad . \quad (26)$$

Multiplying (24) by  $-1 - \log C$ , (25) by  $-1 - \log C'$ , (26) by  $l$ , adding the results, and equating to zero the coefficients of  $\delta n_1, \dots, \delta n'_k$ , we have

$$\begin{aligned} \log n_\lambda - \log C + l \epsilon_\lambda &= 0, \\ \log n'_{\lambda'} - \log C' + l \epsilon'_{\lambda'} &= 0, \end{aligned}$$

whence

$$\left. \begin{aligned} n_\lambda &= C e^{-l \epsilon_\lambda}, \\ n'_{\lambda'} &= C' e^{-l \epsilon'_{\lambda'}} \end{aligned} \right\}$$

*i.e.* the same kind of formulae as before. Since, however,  $l$  appears in both expressions, there is a certain relation between the energies. For the mean kinetic energy of a molecule of a monatomic gas we have found before  $3/2l$ . *The mean kinetic energies of the molecules of the two gases will thus be equal.*

The same method can also be applied to the equilibrium of three, four, or more gases and to cases in which there are external forces. But these cases will here be left on one side.

In applying this method one must always keep in mind that it is based on the assumption that *the results of a lottery can acquaint us with the real state of a system.*

## CHAPTER II

### GIBBS' STATISTICAL METHOD

#### 5. INTRODUCTORY REMARKS

THE probability methods thus far considered have been constructed, because we have at our disposal no mathematical means of following directly and with perfect rigour the play of the molecules and of submitting it to calculations. But the probability methods are based on certain hypotheses, and it cannot be denied that in the formulation of these there is always something arbitrary.

We will now turn our attention to Gibbs' statistical method, of which the basic idea consists in considering a large number, an *assemblage*, of systems in different states or *phases* and submitting these states to statistics. Gibbs distinguishes two kinds of assemblages, viz. *canonical* and *microcanonical* ones. The latter were already introduced by Boltzmann under the name of *ergodes*.

*It is remarkable that the method of microcanonic assemblages or ergodes on the one hand and Boltzmann's probability method on the other hand, which at first sight seem so different, in essence amount to one and the same thing.* We will return to this subject in the sequel.

In statistical mechanics we imagine a very large number ( $N$ ) of systems, copies of one another, each consisting of the same number of molecules, whose positions and velocities, however, differ from system to system. Gibbs comprises the positions and the state of motion of the molecules under the name of a *phase*. Each of the  $N$  systems is thus at a given instant in a certain phase. If  $\Phi$  is some quantity which has for each phase a certain value, as *e.g.* the total energy or the kinetic energy of a system, we can consider the mean value of  $\Phi$  for all the systems of the



assemblage, and this is a quantity which particularly interests us. Or we may ask for the value of  $\Phi$  in that phase which occurs most frequently. There are good reasons for supposing that in this manner we become acquainted with actually *observable* quantities, although the fine molecular structure, differing considerably from system to system, is not thus disclosed to us.

The phase of a system is determined by the general Lagrangian co-ordinates  $q_1 \dots q_s$  and the momenta  $p_1 \dots p_s$ . Here  $s$  is a very large number, for we have to take care of the co-ordinates which determine the position of all molecules and all the small particles they consist of. Each system will be represented by a point in a  $2s$ -dimensional manifold  $q, p$ , with  $q_1 \dots p_s$  as co-ordinates. The volume-element  $dq_1 \dots dp_s$  will be denoted by  $d\lambda$ .

## 6. CANONICAL ASSEMBLAGES

According to Gibbs' definition a canonical assemblage is such that within the element  $d\lambda$

$$Ne^{\frac{\psi - \epsilon}{\Theta}} d\lambda \dots \dots \dots (27)$$

systems are contained,  $N$  being the total number of systems,  $\epsilon$  the energy of a system, and  $\psi$  and  $\Theta$  constants, of which the latter is positive and will be called the modulus of the assemblage.

Thus the density  $F$  of the systems of a canonical assemblage in the  $2s$ -dimensional phase-space will be

$$F = Ne^{\frac{\psi - \epsilon}{\Theta}} \dots \dots \dots (28)$$

Here all values of  $q_1 \dots p_s$  are admissible, similarly those of  $\epsilon$ , while the constant  $\Theta$  characterises the assemblage. Passing to another value of  $\Theta$  we obtain another assemblage. The quantity  $\psi$ , which also is a constant for each assemblage, depends on the modulus  $\Theta$ . In fact, since the integral of (27) extended over all the elements  $d\lambda$  of the phase-space must give the total number  $N$  of systems, we have

$$\int e^{\frac{\psi - \epsilon}{\Theta}} d\lambda = 1,$$

whence

$$e^{\frac{\psi}{\Theta}} = \int e^{-\frac{\epsilon}{\Theta}} d\lambda. \dots \dots \dots (29)$$

If the energy  $\epsilon$  is known as a function of  $q_1 \dots p_s$ , then, for a given  $\Theta$ , the integral has a determined value. Thus, for systems

of a given kind,  $\psi$  is determined by  $\Theta$ . As will appear presently, the latter quantity plays the rôle of the temperature, while  $\psi$  is something like the free energy. From (29) we see at a glance that an additive constant in the energy  $\epsilon$ , which can always be introduced, occurs also in  $\psi$ .

An important theorem is that *a canonical assemblage remains in a stationary state*. While the systems move, their representative points are being displaced, but each element  $d\lambda$  contains permanently the same number of points, though representing different systems.

To prove this theorem we follow the systems in their motion during a certain time  $\tau$ . The systems which at the beginning of this interval were contained in the element  $d\lambda$  will lie at its end in the element  $d\lambda'$ , and by Liouville's theorem,\*

$$d\lambda' = d\lambda.$$

We may say also that all systems, which after the time  $\tau$  lie in  $d\lambda'$ , lay originally in  $d\lambda$ . Thus, after the time  $\tau$  there are in  $d\lambda'$

$$Ne^{\frac{\psi - \epsilon}{\Theta}} d\lambda$$

systems, and before this time there were in the same element

$$Ne^{\frac{\psi - \epsilon'}{\Theta}} d\lambda'$$

systems, where  $\epsilon'$  is the energy corresponding to  $d\lambda'$ .

\* *Proof of Liouville's Theorem.*—Hamilton's equations of motion are

$$\dot{p}_\sigma = -\frac{\partial \epsilon}{\partial q_\sigma}, \quad \dot{q}_\sigma = \frac{\partial \epsilon}{\partial p_\sigma} \quad (\sigma = 1, 2, \dots, s), \quad . \quad . \quad . \quad (a)$$

the energy  $\epsilon$  being expressed as a function of the co-ordinates  $q$  and the momenta  $p$ . Evidently, it suffices to prove the equality of  $d\lambda$  and  $d\lambda'$  for the case of an infinitesimal time  $\tau$ . Now, the values of the co-ordinates and momenta at the end of this time are

$$q'_\sigma = q_\sigma + \dot{q}_\sigma \tau, \quad p'_\sigma = p_\sigma + \dot{p}_\sigma \tau. \quad . \quad . \quad . \quad (b)$$

Again,

$$d\lambda' = \begin{vmatrix} \frac{\partial q'_1}{\partial q_1} & \dots & \frac{\partial p'_s}{\partial q_1} \\ \vdots & & \vdots \\ \frac{\partial q'_1}{\partial p_s} & \dots & \frac{\partial p'_s}{\partial p_s} \end{vmatrix} d\lambda.$$

The elements of this determinant can be derived from (b). Since only the first power of  $\tau$  is retained, we are left with the product of the diagonal elements. Thus the determinant becomes

$$\frac{\partial q'_1}{\partial q_1} \dots \frac{\partial p'_s}{\partial p_s} \left(1 + \frac{\partial \dot{q}_1}{\partial q_1} \tau\right) \dots \left(1 + \frac{\partial \dot{p}_s}{\partial p_s} \tau\right) = 1 + \left(\frac{\partial \dot{q}_1}{\partial q_1} + \dots + \frac{\partial \dot{p}_s}{\partial p_s}\right) \tau,$$

and since the last term vanishes, by (a), we have  $d\lambda' = d\lambda$ .

Now, the state is stationary if

$$Ne^{\frac{\psi - \epsilon'}{\Theta}} d\lambda' = Ne^{\frac{\psi - \epsilon}{\Theta}} d\lambda,$$

and such, in fact, is the case, since  $\epsilon = \epsilon'$  and  $d\lambda = d\lambda'$ .

## 7. SOME THEOREMS ABOUT THE KINETIC ENERGY IN CANONICAL ASSEMBLAGES

We will now apply what precedes to a monatomic gas consisting of  $n$  molecules, whose positions are determined by Cartesian co-ordinates; these will be denoted by  $x_1 \dots x_{3n}$ , while  $\xi_1 \dots \xi_{3n}$  will stand for the velocity components. The phase-space is thus  $6n$ -dimensional, and its element  $d\lambda = dx_1 \dots d\xi_{3n}$  contains

$$Ne^{\frac{\psi - \epsilon}{\Theta}} d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

systems.

The mean value of a quantity  $\Phi$  which depends on the phase will be expressed by

$$\bar{\Phi} = \int e^{\frac{\psi - \epsilon}{\Theta}} \Phi d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

In fact, the mean value is the sum of the  $\Phi$ 's for all  $N$  systems of the assemblage divided by  $N$ , and since all systems contained in  $d\lambda$  have the same value of  $\Phi$ , the contribution due to  $d\lambda$  is  $F\Phi d\lambda$ , so that the formula (31) follows directly from (28). This formula can also be written

$$\bar{\Phi} = \frac{\int e^{-\frac{\epsilon}{\Theta}} \Phi d\lambda}{\int e^{-\frac{\epsilon}{\Theta}} d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

as will be seen by taking account of (29) and remembering that  $\psi$  and  $\Theta$  are constants.

In order to learn something about the kinetic energy, let us calculate the mean value of the squared velocity of a given molecule, say the first molecule, in the different systems. By (32),

$$\overline{\xi_1^2} = \frac{\int \xi_1^2 e^{-\frac{\epsilon}{\Theta}} d\lambda}{\int e^{-\frac{\epsilon}{\Theta}} d\lambda}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

However, treating the question somewhat differently, we will calculate the mean of  $\xi_1^2$  not for *all* systems of the assemblage but

only for those for which  $\xi_1$  may assume all values from  $-\infty$  to  $+\infty$ , while all the remaining quantities are confined to infinitesimal intervals. In fine, we put

$$d\lambda = d\xi_1 d\omega,$$

where  $d\omega$  is an infinitesimal domain of the  $(6n-1)$ -dimensional manifold  $x_1 \dots x_{3n} \xi_2 \dots \xi_{3n}$ , which will be supposed to be constant.

It will be readily seen that also with this new interpretation formula (33) holds good. Now, however, we have to integrate only over  $\xi_1$ . Thus,

$$\overline{\xi_1^2} = \frac{\int \xi_1^2 e^{-\frac{\epsilon}{\Theta}} d\xi_1}{\int e^{-\frac{\epsilon}{\Theta}} d\xi_1}. \quad (34)$$

In  $\epsilon$  is contained also the potential energy  $\epsilon_p$ , but this depends only on the co-ordinates, and since we have limited ourselves to the element  $d\omega$  in which  $\epsilon_p$  has for all systems the same value, both the numerator and the denominator of (34) contain the constant factor,

$$e^{-\frac{\epsilon_p}{\Theta}}.$$

On the other hand, the kinetic energy depends on the velocities and is equal to

$$\frac{1}{2}(m_1 \xi_1^2 + m_2 \xi_2^2 + \dots).$$

Now,  $\xi_2 \dots \xi_{3n}$  are independent of  $\xi_1$  and thus again drop out from the numerator and the denominator, so that we are left only with  $\frac{1}{2}m_1 \xi_1^2$ . Thus we find

$$\overline{\xi_1^2} = \frac{\int_{-\infty}^{+\infty} \xi_1^2 e^{-\frac{m_1 \xi_1^2}{2\Theta}} d\xi_1}{\int_{-\infty}^{+\infty} e^{-\frac{m_1 \xi_1^2}{2\Theta}} d\xi_1} = \frac{\Theta}{m_1} \frac{\sqrt{2\pi\Theta/m_1}}{\sqrt{2\pi\Theta/m_1}} = \frac{\Theta}{m_1}. \quad (35)$$

This result holds for the group of systems contained in  $d\omega$ , but since it is the same for all such groups, it is also valid for the whole assemblage. Thus the mean squared velocity of the first molecule is  $3\Theta/m_1$  and its mean kinetic energy  $\frac{3}{2}\Theta$ . The same

\* Here  $m_1 = m_2 = m_3$ ,  $m_4 = m_5 = m_6$ , and so on.

result holds for the remaining molecules. Consequently the mean kinetic energy of the whole system is

$$\frac{3}{2}n\Theta. \quad (36)$$

We thus see that  $\Theta$  plays the part of the absolute temperature, as was mentioned before.

Returning to Gibbs' considerations, let us now fix our attention upon an assemblage of  $N$  systems with the general co-ordinates  $q_1 \dots q_s$  and momenta  $p_1 \dots p_s$ .

For this assemblage we will prove a theorem in which the formula (35) concerning a gas is contained as a particular case. Suppose that a co-ordinate  $\eta$  (belonging to the set  $q_1 \dots p_s$ ) occurs in  $\epsilon$  only through a term of the form  $\frac{1}{2}c\eta^2$ . What is the value of  $\frac{1}{2}c\eta^2$ ? Let us separate the term  $\frac{1}{2}c\eta^2$  from  $\epsilon$  and call  $\epsilon'$  the sum of the remaining terms, and similarly the factor  $d_\eta$  from  $d\lambda$ , denoting the product of the remaining differentials by  $d\lambda'$ . Then

$$\epsilon = \frac{1}{2} c \eta^2 + \epsilon' \text{ and } d\lambda = d\eta d\lambda',$$

and, by our general formula (32) for  $\overline{\Phi}$ ,

$$\overline{\eta^2} = \frac{\int e^{-\frac{\frac{1}{2}c\eta^2 + \epsilon}{\ominus}} \eta^2 d\eta d\lambda'}{\int e^{-\frac{\frac{1}{2}c\eta^2 + \epsilon}{\ominus}} d\eta d\lambda'} = \frac{\int_{-\infty}^{+\infty} e^{-\frac{c\eta^2}{2\ominus}} \eta^2 d\eta}{\int_{-\infty}^{+\infty} e^{-\frac{c\eta^2}{2\ominus}} d\eta} = \frac{\ominus}{c}, \quad (37)$$

$$i.e. \quad \overline{\frac{1}{2}c\eta^2} = \frac{1}{2}\Theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

whence (35) follows at once.

This general result can be applied, for instance, to a velocity component of the centre of gravity of a particle endowed with Brownian movement, or also to a component of its rotational velocity. Suppose that such a particle can rotate about a fixed axis and that it is acted upon by a restituting couple, proportional to the angle of rotation. Then the theorem will hold for the mean potential energy.

The result (38) can also be applied to a Planckian resonator. If this resonator is linear and the above considerations hold for it, then the mean value of its potential as well as of its kinetic energy is equal to  $\frac{1}{2}\Theta$ .

Further, it can readily be proved that also in the case of a gas consisting of unequal molecules the mean kinetic energy corresponding to the motion of the centre of gravity of a given

molecule in the direction of one of the co-ordinates, and taken for all the systems of the assemblage, has the value  $\frac{1}{2}\Theta$ . This holds good even for the mean energy belonging to the motion of the centre of gravity of an arbitrary *group* of molecules. The proof is as follows :

Let us consider  $k$  molecules and let us fix our attention upon the  $x$ -components of the motion of their centres of gravity as given by their momenta  $p_1 \dots p_k$  (these belong to the set  $p_1 \dots p_s$ ). Then the  $x$ -component of the velocity of the centre of gravity of all these molecules will be

$$\xi = \frac{p_1 + \dots + p_k}{m_1 + \dots + m_k},$$

so that

$$\overline{\xi^2} = \frac{1}{(\Sigma m)^2} \{ \overline{p_1^2} + \dots + \overline{p_k^2} + 2\overline{p_1 p_k} + \dots \}.$$

Now, it can be shown that all terms such as  $\overline{p_1 p_k}$  vanish. Again, by (35),

$$\overline{p_1^2} = m_1 \Theta.$$

Thus,

$$\overline{\xi^2} = \frac{1}{(\Sigma m)^2} (m_1 \Theta + \dots + m_k \Theta) = \frac{\Theta}{\Sigma m}$$

$$\text{or} \quad \frac{1}{2}(\Sigma m) \overline{\xi^2} = \frac{1}{2}\Theta, \quad . \quad . \quad . \quad . \quad (39)$$

which is the required expression, analogous to (38). It reads : *The mean kinetic energy of the centre of gravity of a group of molecules is equal to the mean kinetic energy of a single molecule.*

All that has hitherto been said about the canonical assemblages holds for every system, consisting of any number of particles, even if this number be small.\* Henceforth, however, we will assume that the number  $n$  of material particles in a system is very great, as is *e.g.* the number of molecules in an ordinary lump of matter. In that case the canonical distribution has the remarkable property that, although within the assemblage all possible phases are represented, yet the overwhelming majority of systems, so far as observable quantities are concerned, do not perceptibly differ from each other. This cannot in general be proved

\* In connection with Boltzmann's method the number of particles is supposed to be very great,



rigorously, but what can thus be proved is that the total value of the kinetic energy for the  $n$  particles or for a very great number  $k$  of chosen particles varies within the assemblage but very little.

The averaged total kinetic energy of these  $k$  selected particles is, by (38), equal to  $\frac{3}{2}k\Theta$ , and we have now to prove that in the great majority of systems no noteworthy deviations from this value occur.

*Proof.* If  $p_1 \dots p_{3k}$  be the components of the momenta of the  $k$  particles, the element  $dS$  of Gibbs' phase-space ( $q_1 \dots p_s$ ) can be split into two factors, the element  $d\mu$  of the manifold  $p_1 \dots p_{3k}$ , and another element  $d\lambda$  of the manifold ( $q_1 \dots q_{3n}, p_{3k+1} \dots p_{3n}$ ) determined by the remaining co-ordinates, thus :

$$dS = d\mu d\lambda.$$

By (27) the number of systems in  $dS$  is

$$Ne^{\frac{\psi - \epsilon}{\Theta}} dS.$$

Let us split  $\epsilon$  into two parts, one corresponding to  $p_1 \dots p_{3k}$  and another which will be denoted by  $\epsilon'$ , so that

$$Ne^{\frac{\psi - \epsilon}{\Theta}} dS = Ne^{\frac{1}{\Theta} \left[ \psi - \left( \frac{p_1^2}{2m_1} + \dots + \frac{p_{3k}^2}{2m_{3k}} \right) - \epsilon' \right]} d\mu d\lambda.$$

We allow the remaining co-ordinates (*i.e.* with the exclusion of  $p_1 \dots p_{3k}$ ) to assume all possible values and we seek the number of systems contained in  $dS$ . In fine, we integrate over  $d\lambda$ . Thus we obtain an expression of the form

$$CNe^{-\frac{1}{2\Theta} \left( \frac{p_1^2}{m_1} + \dots + \frac{p_{3k}^2}{m_{3k}} \right)} d\mu,$$

where  $C$  is a constant whose value can be determined by noting that an integration of this expression over  $p_1, \dots, p_{3k}$  must give the number  $N$ .

By means of this artifice we got rid of the remaining variables and we have now to do only with the momenta of our  $k$  particles. We ask in how many systems does the total kinetic energy  $\frac{1}{2} \left( \frac{p_1^2}{m_1} + \dots + \frac{p_{3k}^2}{m_{3k}} \right)$  of these particles lie between  $u$  and  $u + du$ .

To answer this question we consider the  $3k$ -dimensional space ( $p_1 \dots p_{3k}$ ). In this space the representative points of the systems possessing the energy  $u$  will lie upon a certain surface,

and those with the energy  $u + du$  will lie upon another surface surrounding the latter. Our problem consists in determining the number of points in the thin shell contained between these two surfaces. This number will be equal to the volume of the shell multiplied by the density of the points. The volume, which will be proportional to  $du$ , can be written  $I du$ , where  $I$  is some function of  $u$ . Thus the number of points within the shell will be

$$C N e^{-\frac{u}{\Theta}} I du. \quad (40)$$

In this expression  $I du$  can be considered as the difference of two volumes,  $K(u + du)$  and  $K(u)$ , where  $K(u)$  is the volume of that part of the space ( $p_1 \dots p_{3k}$ ) in which the energy is smaller than  $u$ . This volume can be easily proved to be proportional to  $u^{\frac{3}{2}k}$ . Put  $K(u) = C' u^{\frac{3}{2}k}$ . Then

$$I du = C' \frac{3}{2} k u^{\frac{3}{2}k-1} du, \quad (41)$$

where  $q = \frac{3}{2}k - 1$ .

The number of points within the shell, and therefore also the required number of systems, thus becomes

$$\frac{3}{2} k C C' N u^q e^{-\frac{u}{\Theta}} du. \quad (42)$$

The factor of  $du$  can be represented graphically as a function of  $u$ .

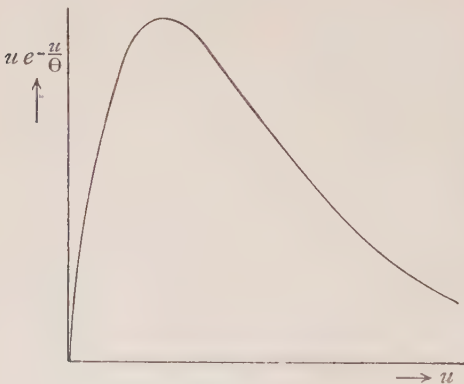


FIG. 1.

This gives a curve resembling somewhat that corresponding to Maxwell's law (Fig. 1). There is, however, this difference, that while Maxwell's formula contains the expression  $u e^{-\frac{u}{\Theta}}$  corresponding to  $q=1$ , in the present case  $q$  is a large number so that the character of the curve is changed, its top being now very sharp

(Fig. 2). This means that *almost all systems possess very nearly the same energy*, viz. that represented by  $AB$ .

That the top of the curve is very sharp can be proved as follows.

The variable  $u$  in (42) being replaced by

$$\omega = \frac{u}{q\Theta},$$

the number of systems within the shell becomes

$$C''N(\omega e^{-\omega})^q d\omega, \quad . \quad . \quad . \quad . \quad (43)$$

where  $C''$  embodies all the constant factors. The expression  $\omega e^{-\omega}$  attains a maximum for  $\omega = 1$  and vanishes for  $\omega = 0$  and  $\omega = \infty$ . Now, when this expression (to which the ordinate of Fig. 1 is proportional) is raised to a higher and higher power, the maximum ordinate will more and more exceed the other ordinates and the top of the curve will become always sharper. Even the ordinates next to  $\omega = 1$  can be made as small as we please by making  $q$  (or  $k$ ) large enough. Again, with increasing  $q$  the integral

$$\int_0^\infty C''N(\omega e^{-\omega})^q d\omega, \quad . \quad . \quad . \quad . \quad (44)$$

representing the total number of systems, is more and more reduced to items contributed by a very narrow interval in the immediate neighbourhood of  $\omega = 1$ .

Ultimately, since  $u = q\Theta\omega$ , we find for the kinetic energy which almost all systems of  $k$  particles will thus very nearly possess

$$q\Theta = (\frac{3}{2}k - 1)\Theta,$$

or,  $k$  being very large,

$$\frac{3}{2}k\Theta,$$

as might have been expected.

What has just been proved for a selected group of  $k$  particles holds, of course, also for the whole system. The remarkable feature of all this is that we have now proved rigorously

that, so far as the kinetic energy is concerned, all systems of a canonic assemblage are nearly repetitions of each other.

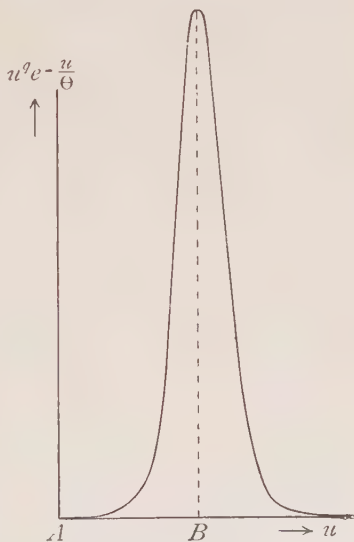


FIG. 2.

If this were not so, not much could be accomplished with Gibbs' systems. In accordance with Gibbs' considerations it can be assumed that also the potential energy and other quantities bearing upon a great number of particles (or what we have called "observable quantities") have in the overwhelming majority of systems approximately the same values, although this cannot be proved rigorously even in the case of, say, the total energy.

### 8. MICROCANONIC ASSEMBLAGES

Although in the phase-space a variety of values of  $\epsilon$  are represented, a given system retains always the same  $\epsilon$ ; while the quantities  $q_1, \dots, p_s$  vary, the system moves not over the whole space but only over a sub-manifold whose number of dimensions is a unit lower. In fact, we can imagine that all points corresponding to a given value of  $\epsilon$  lie upon a "surface", the energy surface. Further, for different values of  $\epsilon$  a number of such surfaces, surrounding each other, can be constructed. In each infinitely thin layer contained between two such surfaces  $\epsilon$  can be considered as constant. The rate at which the density in a canonical assemblage, viz.  $Ne^{\frac{\psi - \epsilon}{\Theta}}$ , diminishes with increasing  $\epsilon$  depends on the modulus  $\Theta$ . A large  $\Theta$  will favour the occurrence of large energies.

Let us fix our attention upon a given value of  $\epsilon$ . Let  $V$  be the volume of that part of the phase-space in which  $\epsilon$  is smaller than the given value. The value of  $V$  will depend only on the nature of the systems.

If  $V$  be known [as function of  $\epsilon$ ], the volume of the layer contained between two energy surfaces can be written

$$\frac{dV}{d\epsilon}d\epsilon,$$

and the number of systems possessing an energy contained between  $\epsilon$  and  $\epsilon + d\epsilon$  will be

$$Ne^{\frac{\psi - \epsilon}{\Theta}} \frac{dV}{d\epsilon} d\epsilon. \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Gibbs puts for the sake of simplicity

$$\frac{dV}{d\epsilon} = e^\phi \quad \text{or} \quad \phi = \log \frac{dV}{d\epsilon}. \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Thus the number of systems becomes

$$Ne^{\frac{\psi - \epsilon}{\Theta} + \phi} d\epsilon. \quad . \quad . \quad . \quad . \quad (47)$$

If  $V$  is known as a function of  $\epsilon$ , so also is  $\phi$ . We have found that almost all systems have nearly the same energy, and we can now say that this will be the energy  $\epsilon = \epsilon_m$  for which

$$Ne^{\frac{\psi - \epsilon}{\Theta} + \phi}$$

attains a maximum. The condition for this maximum is

$$\left(\frac{d\phi}{d\epsilon}\right)_{\epsilon = \epsilon_m} = \frac{1}{\Theta}. \quad . \quad . \quad . \quad . \quad (48)$$

This differential equation gives us the energy which occurs most frequently in a canonical assemblage of modulus  $\Theta$ . But to solve the equation,  $\phi$  must be known as a function of  $\epsilon$ .

Again, by (46) and (48),

$$\Theta = \frac{\left(\frac{dV}{d\epsilon}\right)_{\epsilon = \epsilon_m}}{\left(\frac{d^2V}{d\epsilon^2}\right)_{\epsilon = \epsilon_m}}. \quad . \quad . \quad . \quad . \quad (49)$$

This is the value which must be given to  $\Theta$  in order that  $\epsilon$  shall have a determined value  $\epsilon_m$ .

Since for a given  $\Theta$  there are no noteworthy deviations from a particular value of  $\epsilon$ , all points of a canonical assemblage will lie next to a certain surface and even at a short distance from that surface almost no further points will be found. In other words, nearly all points are crowded in a very thin layer  $d\epsilon$ , and those outside it can, in view of their extreme scarcity, be left out of account. An assemblage is called *microcanonical* if *all* its points lie in an infinitely thin layer  $d\epsilon$  and are distributed over it with equal density. Thus the points of a canonical assemblage which lie in the layer  $d\epsilon$  form a microcanonical assemblage (in fact, the density  $Ne^{\frac{\psi - \epsilon}{\Theta}}$  is constant throughout such a layer). That a canonical assemblage can thus be built up of a great number of microcanonical ones, might have been said prior to the considerations of Article 7. Now, however, having learned from these considerations that, owing to the large number of molecules, practically all the points of a canonical assemblage lie in a thin

layer along the surface  $\epsilon_m$ , we can conclude that a *canonical assemblage is equivalent to a single microcanonical assemblage*. The boundary of the layer is sharp in the case of the latter, and diffuse in that of the former, but this makes no great difference.

A canonical assemblage is characterised by the modulus  $\Theta$ ; a microcanonical assemblage has no modulus but is determined by the value of  $\epsilon$ . The connection between a canonical assemblage of modulus  $\Theta$  and the corresponding microcanonical assemblage with the energy  $\epsilon$  is given by (48).



## CHAPTER III

### CONNECTION BETWEEN BOLTZMANN'S METHOD, GIBBS' METHOD, AND EINSTEIN'S VIEWPOINT

#### 9. EQUIVALENCE OF LOTTERY AND MICROCANONIC ASSEMBLAGE

AFTER all that has been said about the methods of Boltzmann and of Gibbs we can prove that they are equivalent.

We consider for this purpose a system of  $n$  molecules. Each molecule has  $s$  co-ordinates ( $q$ ) and  $s$  momenta ( $p$ ), and will thus be represented by a point in the  $2s$ -dimensional space ( $q_1 \dots p_s$ ). We divide this space into equal volume-elements  $dS_1 \dots dS_\kappa \dots dS_k$ .

Let us again draw lots in the previously explained manner for each molecule separately. An "experiment" determines entirely the state of the system, and a number of repetitions of such experiments gives us as many different states of the system, so that we get an "assemblage". In our previous considerations (cf. page 146) only those experiments counted which gave a determined value for the energy  $\epsilon$  (one perceives here already an analogy with the microcanonic assemblage). We will now put the condition somewhat broader and require that  $\epsilon$  should lie between two arbitrary limits  $\epsilon_1$  and  $\epsilon_2$ , thus

$$\epsilon_1 < \epsilon < \epsilon_2.$$

We have just spoken of the elements  $dS_1$ , etc., of a phase-space in which the state of a single molecule is represented by a point. Now, such a space can be introduced for each molecule and all these spaces can be compounded into a single, more-dimensional space whose point will represent the state of all molecules (*i.e.* the outcome of an "experiment"). The latter space is nothing else than Gibbs' phase-space. Its element will be the product of a number of elements, each belonging to one of

the constituent [molecular] spaces, and since the latter are supposed to be divided into equal volume-elements, the volume-elements  $d\lambda$  of Gibbs' phase-space will again be all equal.

Let us now see what will be the outcome of such a repeated drawing of lots subject to the condition  $\epsilon_1 < \epsilon < \epsilon_2$ . For each molecule the chances of falling into one or another element of its proper space are equal, and which element is to be allotted to one molecule is entirely independent of which element has been occupied by another molecule. Consequently, the probability that the point representing the state of a system shall lie in a given element  $d\lambda$  is equal for all elements, and if we make so many experiments that even each element  $d\lambda$  contains a great number of points, then in the assemblage the system points are distributed throughout with the same density. The assemblage is, by assumption, limited to a layer contained between the surfaces which correspond to the energies  $\epsilon_1$  and  $\epsilon_2$ , and within this layer the density of the system points is constant. We can always assume that the elements of the constituent [molecular] spaces and therefore also the elements  $d\lambda$  are so small, that in the said layer there are still very many elements  $d\lambda$ .

If we now allow the difference  $\epsilon_2 - \epsilon_1$  to tend to zero, we shall approach, on the one hand, the lottery with the previous condition that only those experiments should count which yield a determined value of the energy and, on the other hand, the microcanonic assemblage. *We can thus say that Gibbs' microcanonic assemblage is nothing else than a graphical representation of the results of Boltzmann's lottery.*

#### 10. REMARKS ON SOME SUBTLETIES WHICH MAY OCCUR

The preceding considerations call for a few further remarks. Following Boltzmann's method we have supposed in Article 3 that it is being determined by means of a lottery how many molecules should be placed in each element of the space ( $q_1 \dots p_s$ ). In the case of monatomic molecules this space, which is six-dimensional, splits into two three-dimensional ones. We then determine by drawing lots the distribution of velocities and the density in each volume-element of the gas without troubling ourselves about the manner in which the particles are placed in each element. There are cases, however, in which such a knowledge

may be desirable. Thus it may be of importance to know to what extent the molecules can be considered as free and to what extent they are bound, say, two by two, to each other, or, at least, if there can be no question of a fixed binding, what proportion of the particles approach each other so closely as to attract themselves perceptibly (*e.g.* to revolve about each other). Again, if the particles are considered simply as elastic spheres, the question arises as to how many pairs of particles lie at such a small distance that they have just collided or will presently collide with each other, how many are separated by larger distances, etc.

If we are to answer such questions we evidently can no longer content ourselves with considering volume-elements which still contain many molecules.

In the theory of microcanonic assemblages similar difficulties are met with by making the elements  $d\lambda$  so small that, *e.g.*, the interval allowed for the co-ordinates of the centre of a molecule within such an element shall be small compared with the diameter of the molecules. Systems in which a certain pair of particles is in mutual contact and systems in which the distance of these particles is, say, a hundredth of their diameter are then placed, even for equal velocities, in different elements  $d\lambda$ . They are separated from each other in the statistics of the assemblage. On this "finer scale" also a canonical assemblage could be represented.

When the problem is thus approached, the case of molecules of constant volume and impenetrable to each other can be treated in different ways. In the first place we can simply say that a configuration in which the distance of the centres of two molecules is smaller than their diameter does not occur. This amounts to declaring certain positions of the system point, *i.e.* certain portions of the phase-space, as impossible and excluding them. But the matter can also be dealt with in a different way, *viz.* by allowing some approach of the centres below the said distance, but assuming at the same time that this is opposed by great repulsive forces. Then, without giving rise to difficulties, also such positions can be admitted to the canonical assemblage. The reason why this entails no difficulty is that to the repulsive forces corresponds a potential energy which, being assumed to be nil for particles which lie outside each other, is in the present case positive and very large, provided the forces opposing an inter-

penetration of the particles are very great. Now, wherever the potential and thus also the total energy becomes very large, the density of the systems in a canonical assemblage is, by (27), exceedingly small, that is to say, although systems with abnormal energies do occur in a canonical assemblage, yet they are so scarce that they can entirely be left out of account.

From this point of view the case of a microcanonic assemblage is quite simple. In fact, we then have to do with a distribution of system points over a surface  $\epsilon$  or over a thin layer  $(\epsilon, \epsilon + d\epsilon)$ , and from that surface or that layer the abnormal systems are ruled out automatically, since they would imply a much too large energy.

## 11. STATISTICAL DEFINITION OF ENTROPY

We have proved that a microcanonic assemblage is a graphical representation of the outcome of a lottery. This leads at once to the following conclusion. Suppose we require the probability  $w$  that a drawing of lots should yield a certain case (enclosed between given limits); this probability is equal to the number of drawings which give that case, divided by the total number of drawings. The former ("favourable") drawings are represented by points which lie within a certain part of the phase-space, and  $w$  is the volume of that part divided by the volume of the whole phase-space under consideration.

The state which arises when the system is left to itself will be characterised by a maximum of  $w$ . For we suppose that the system will always tend to the most probable state.

Instead of making  $w$  a maximum we may as well make

$$H = -\log w$$

a minimum, and *this  $H$  is nothing else than the function  $H$  appearing in a famous theorem of Boltzmann.* We shall return to this subject in Chapter V.

*Now, we arrive at the most general definition of entropy by making it equal or proportional to the logarithm of the probability  $w$ .* We need not trouble, of course, about an additive constant for  $\log w$ , or a multiplicative one for  $w$ . Thus we write for the entropy

$$\eta = k \log w. \quad . \quad . \quad . \quad . \quad . \quad (50)$$

It will appear later that, in order to bring this definition into harmony with the usual thermodynamical definition, we must put

$$k = \frac{2}{3}\alpha,$$

where  $\alpha$  is the well-known universal constant appearing in the expression  $\alpha T$  for the mean kinetic energy of a gas molecule. Accordingly,  $k$  is "Planck's constant".

$$\text{Thus,} \quad \eta = \frac{2}{3}\alpha \log w.$$

Now, for a gram molecule of a gas, containing  $N$  molecules, we have

$$pv = \frac{2}{3}\alpha TN.$$

If we introduce the gas constant for a gram molecule, viz.  $R = pv/T$ , then

$$\frac{2}{3}\alpha N = R,$$

$$\text{and} \quad \eta = \frac{R}{N} \log w. \quad . \quad . \quad . \quad . \quad . \quad (51)$$

*This is what Einstein calls Boltzmann's principle.*

## 12. EINSTEIN'S TREATMENT \*

Einstein considers the matter from a somewhat different point of view.

He says : If a system is left to itself during a sufficiently long time, it will pass through *all* the states which are compatible with the given value of its energy. Then all possible states, no matter how improbable in themselves, will sooner or later occur. The system describes in the phase-space a line. Now, adopting this point of view, let us seek the probability of a given state (contained within narrow limits). This probability will be

$$\frac{\tau}{\theta},$$

where  $\theta$  is a very long time and  $\tau$  that part of it during which the state in question prevails.

*But also this concept amounts essentially to the same thing as a microcanonic assemblage. Now,*

\* A. Einstein, *Ann. der Physik* (4), xxxiii., 1910, p. 1275.



In fact, as was just said, the system describes in the phase-space a certain line (cf. Fig. 3). Let  $A$  and  $A'$ ,  $B$  and  $B'$  be its positions on this line at the instants  $t$  and  $t'$ ,  $t + \tau$  and  $t' + \tau$  respectively.

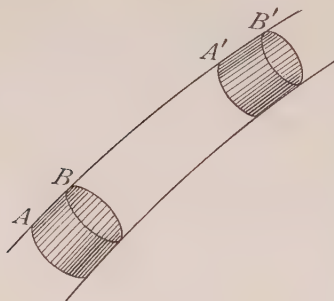


FIG. 3.

Now, according to Einstein, the probability that the system shall lie between  $A$  and  $B$  is the same as the probability that it shall lie between  $A'$  and  $B'$ . Let us take a tube of such lines in the immediate neighbourhood of  $AA'$ , and let  $d\lambda$  and  $d\lambda'$  be the elements of this tube extending

from  $A$  to  $B$  and from  $A'$  to  $B'$ . Then we can prove by Liouville's theorem that  $d\lambda = d\lambda'$ . Thus for equal elements the probability is the same, exactly as in a microcanonic assemblage. (The tube lies, of course, *within* the thin layer of the microcanonic assemblage.)

*The graphical representation of Einstein's concept yields thus again a microcanonic assemblage.*

### 13. SUMMARY

To sum up what precedes we can say that we have considered three different methods which can be adopted in order to weigh against each other the probabilities of different states, viz. :

- 1°. Gibbs' microcanonic assemblage,
- 2°. Boltzmann's lottery,
- 3°. Einstein's time-assemblage,

and have found that these three methods are equivalent.



## CHAPTER IV

### CONNECTION BETWEEN ENTROPY AND PROBABILITY, TREATED BY GIBBS' METHOD

#### 14. GENERALISATION OF THE STATISTICAL DEFINITION OF ENTROPY

Our further considerations will be based upon a microcanonic assemblage, with the understanding that this is not spread over a single surface but is contained in a thin layer  $d\epsilon$  in the  $2s$ -dimensional space, corresponding to the energy limits  $\epsilon$  and  $\epsilon + d\epsilon$ .

These limits being fixed, there is still a variety of possible states, and the probability of one of them (within certain limits), *i.e.* the probability that the point representing the state should lie within a given element  $A$  of the layer  $d\epsilon$ , can be taken to be expressed by the number of points in  $A$  divided by the total number of points in the layer  $d\epsilon$ .

Since the density of the points is constant throughout the layer, this probability can also be defined as

$$\frac{\text{the volume of } A}{\text{total volume of the layer } d\epsilon}.$$

The entropies of the different states, always within the fixed energy limits, could then be put proportional to the logarithms of their probabilities.

We prefer, however, to shape the statistical definition of entropy somewhat differently, so that it will enable us to compare entropies at different values of the energy, always for equilibrium states of the system. We shall thus have something analogous to the thermodynamical treatment in which the entropy is likewise considered as a function of the energy (and of "parameters" such as the volume).

Our new definition is as follows: In order to determine the entropy  $\eta$  for a given energy  $\epsilon$  and, *e.g.* a given volume, we seek the size of that part of Gibbs' phase-space which corresponds to this volume and to an energy contained between  $\epsilon$  and  $\epsilon + d\epsilon$ . If this size be  $Kd\epsilon$ , then the entropy is

$$\eta = \frac{R}{N} \log K, \quad . \quad . \quad . \quad . \quad . \quad (52)$$

apart from an arbitrary additive constant.

### 15. EQUIVALENCE OF THE GENERALISED STATISTICAL AND THE THERMODYNAMICAL DEFINITION OF ENTROPY, PROVED FOR A GAS

We will calculate the quantity  $K$  for a monatomic gas consisting of  $n$  molecules which do not attract each other and whose dimensions are disregarded (so that  $a$  and  $b$  in van der Waals' formula vanish). Let  $v$  be the volume of the gas and let its energy be contained between  $\epsilon$  and  $\epsilon + d\epsilon$ .

Let  $x_1, \dots, x_{3n}$  be the co-ordinates and  $p_1, \dots, p_{3n}$  the momenta. We will first calculate the size of that portion of the phase-space for which the volume of the gas has the given value  $v$  and the energy is contained between 0 and  $\epsilon$ . This is

$$L = \int dx_1 \dots dx_{3n} \int dp_1 \dots dp_{3n}, \quad . \quad . \quad . \quad (53)$$

the limits of the integral being determined by the given values of  $v$  and  $\epsilon$ .

Since the integral over the three co-ordinates of the first molecule, taken for all possible values of these co-ordinates, is equal to the volume of the gas, *i.e.*

$$\iiint dx_1 dx_2 dx_3 = v,$$

and similarly for the remaining molecules, we have

$$\int dx_1 \dots dx_{3n} = v^n, \quad . \quad . \quad . \quad . \quad (53a)$$

$$\text{so that} \quad \int dx_1 \dots dx_{3n} \int dp_1 \dots dp_{3n} = v^n \int dp_1 \dots dp_{3n}. \quad . \quad . \quad . \quad (54)$$

$$\text{Since} \quad \epsilon = \frac{1}{2m} (p_1^2 + \dots + p_{3n}^2),$$

the integral  $\int dp_1 \dots dp_{3n}$  represents the volume of a sphere of

radius  $\sqrt{2m\epsilon}$  in the  $3n$ -dimensional space. Now, the volume of a sphere of radius  $a$  in an  $s$ -dimensional space is

$$\frac{\pi^{\frac{1}{2}s}}{\Gamma(\frac{1}{2}s + 1)} a^s,$$

where  $\Gamma$  is the gamma function. Thus

$$L = \frac{\pi^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n + 1)} (2m\epsilon)^{\frac{3}{2}n} v^n.$$

Since  $Kd\epsilon$  is the difference of the values of  $L$  which correspond to the values  $\epsilon$  and  $\epsilon + d\epsilon$  of the energy, we have

$$K = \frac{3}{2}n \frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n + 1)} \epsilon^{\frac{3}{2}n-1} v^n. \quad (55)$$

Hence, by (52),

$$\eta = \frac{R}{N} \left\{ \log \left( \frac{3n}{2} \right) + \frac{3n}{2} \log (2\pi m) - \log \Gamma \left( \frac{3n}{2} + 1 \right) + \left( \frac{3n}{2} - 1 \right) \log \epsilon + n \log v \right\}. \quad (56)$$

But since an additive constant in the expression for the entropy is irrelevant, we can cancel the first three terms within the brackets, so that we are left with

$$\eta = \frac{R}{N} \left\{ \left( \frac{3}{2}n - 1 \right) \log \epsilon + n \log v \right\}. \quad (57)$$

Again, we may without any serious objection cancel 1 in presence of  $\frac{3}{2}n$ . Thus we have ultimately

$$\eta = \frac{R}{N} \left\{ \frac{3}{2}n \log \epsilon + n \log v \right\}. \quad (58)$$

*This expression is, indeed, equivalent to the thermodynamical definition of entropy, which can be proved, for instance, by showing that the usual relations*

$$\frac{\partial \eta}{\partial \epsilon} = \frac{1}{T} \quad \text{and} \quad \frac{\partial \eta}{\partial v} = \frac{p}{T}$$

can also be derived from that expression. Now, differentiating (58) with respect to  $\epsilon$ , we have

$$\frac{\partial \eta}{\partial \epsilon} = \frac{3}{2} \frac{nR}{N},$$

and substituting  $\frac{R}{N} = \frac{2}{3}a$ ,

$$\frac{\partial \eta}{\partial \epsilon} = \frac{an}{\epsilon} = \frac{an}{anT} = \frac{1}{T} \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Again, 
$$\frac{\partial \eta}{\partial v} = \frac{Rn}{Nv} = \frac{2an}{3v} = \frac{2anT}{3vT} = \frac{p}{T} \quad . \quad . \quad . \quad . \quad . \quad (60)$$

Thus  $\eta$  as given by (58) is the "thermodynamical" entropy.

#### 16. PROOF OF THE SAID EQUIVALENCE FOR ANY BODY WHOSE STATE IS DETERMINED BY THE VOLUME AND THE ENERGY

Suppose we have two bodies which consist of molecules and which cannot mix with each other, being, *e.g.*, separated by a very thin piston (occupying no volume) which can be moved without friction. Let this piston be a good conductor of heat.

The quantities belonging to the two bodies taken separately will be distinguished by the suffixes 1 and 2.

The total energy of the whole system being contained between  $\epsilon$  and  $\epsilon + d\epsilon$ , and the total volume  $v$  being fixed, we ask: What is the most probable position of the piston and how will the energy distribute itself between the two bodies?

To solve this problem we imagine a microcanonic assemblage. The phase-space of the whole system has for its co-ordinates the co-ordinates and the momenta of the molecules of both bodies 1 and 2, and can thus, as before, be split into two spaces, so that the product of two volume-elements of the latter gives a volume-element of the former.

Now, suppose that while the volumes of the two bodies are  $v_1$  and  $v_2$  and the total energy is contained within the limits  $\epsilon$  and  $\epsilon + d\epsilon$ , the energy of the first body is contained between  $\epsilon_1$  and  $\epsilon_1 + d\epsilon_1$ . Let  $G$  be the region of the compound phase-space corresponding to these conditions.

To find  $G$  we take first  $\epsilon_1$  and  $\epsilon_1 + d\epsilon_1$  for the energy limits of the first, and  $\epsilon_2$  and  $\epsilon_2 + d\epsilon_2$  for those of the second body ( $\epsilon_1 + \epsilon_2 = \epsilon$ ). By what was said in Article 14, to these conditions will correspond portions

$$K_1(\epsilon_1, v_1)d\epsilon_1 \text{ and } K_2(\epsilon_2, v_2)d\epsilon_2$$

of the partial spaces and therefore a region

$$K_1(\epsilon_1, v_1)K_2(\epsilon_2, v_2)d\epsilon_1d\epsilon_2 \quad . \quad . \quad . \quad (60a)$$

of the compound phase-space. In order to find  $G$ ,  $d\epsilon_1 d\epsilon_2$  has to be replaced by  $d\epsilon_1 d\epsilon$  and (60a) has to be divided by the functional determinant of  $\epsilon_1$  and  $\epsilon$  with respect to  $\epsilon_1$  and  $\epsilon_2$ , which, however, is equal to unity. Thus \*

$$G = K_1(\epsilon_1, v_1) K_2(\epsilon_2, v_2) d\epsilon_1 d\epsilon. \quad (60b)$$

As "the most probable" state, and we will suppose that this is also the real state of the system, can be considered that for which  $\epsilon_1$  and  $v_1$  are such that

$$K_1(\epsilon_1, v_1) K_2(\epsilon_2, v_2)$$

is a maximum. We may also make a maximum the logarithm of this expression or, by formula (52), applicable to both bodies, the sum of the statistical entropies

$$\eta_1 + \eta_2.$$

Thus we find, as the first condition :

$$\frac{\partial \eta_1}{\partial \epsilon_1} \delta \epsilon_1 + \frac{\partial \eta_2}{\partial \epsilon_2} \delta \epsilon_2 = 0,$$

or, since  $\delta \epsilon_2 = -\delta \epsilon_1$ ,

$$\frac{\partial \eta_1}{\partial \epsilon_1} = \frac{\partial \eta_2}{\partial \epsilon_2}, \quad (61)$$

and similarly, as the second condition :

$$\frac{\partial \eta_1}{\partial v_1} = \frac{\partial \eta_2}{\partial v_2}. \quad (62)$$

In these formulae  $\eta_1$  and  $\eta_2$  are the statistical entropies. But these equations can serve to show that the identity of the thermodynamical and the statistical entropy, which has already been proved for a gas, holds good also for any other body. For this purpose we will suppose that one of the two bodies, say the second, is a gas, at temperature  $T$  and pressure  $p$ . Then, by (59) and (61),

$$\frac{\partial \eta_1}{\partial \epsilon_1} = \frac{1}{T}. \quad (63)$$

This condition being satisfied, the body 1 can be in equilibrium with the gas of temperature  $T$ , and has thus *itself* this tempera-

\* The transition from (60a) to (60b) can be made clear by a diagram in which  $\epsilon_1$  and  $\epsilon_2$  are represented by rectangular co-ordinates.

ture. Hence the relation (59) between the temperature and  $\partial\eta_1/\partial\epsilon_1$  holds also for any body. Again, by (60) and (62),

$$\frac{\partial\eta_1}{\partial v_1} = \frac{p}{T}, \quad . \quad . \quad . \quad . \quad . \quad (64)$$

whence we can draw a similar conclusion as from (63), namely, that the relation (60) holds for any body (for, if  $p$  be the pressure of a gas with which a body is in equilibrium,  $p$  will also be the pressure of that body).

All this is valid for a perfectly arbitrary body 1. Thus we can conclude that, for *every* body,

$$\frac{\partial\eta}{\partial\epsilon} = \frac{1}{T} \quad . \quad . \quad . \quad (64) \quad \text{and} \quad \frac{\partial\eta}{\partial v} = \frac{p}{T} \quad . \quad . \quad . \quad (65)$$

For a simultaneous variation of the volume and the energy we have

$$d\eta = \frac{\partial\eta}{\partial\epsilon}d\epsilon + \frac{\partial\eta}{\partial v}dv$$

$$\text{or} \quad d\eta = \frac{1}{T}d\epsilon + \frac{p}{T}dv = \frac{dQ}{T}, \quad . \quad . \quad . \quad . \quad (66)$$

where  $dQ$  is the heat to be supplied.

The equations (64), (65), and (66), which have been here deduced for the statistical entropy of a wholly arbitrary body, are perfectly analogous to those for the thermodynamical entropy known from classical thermodynamics.

In connection with this subject an interesting question arises. Suppose that in the most probable state of our system of two bodies the energy of the first is  $\epsilon_{10}$  and that of the second  $\epsilon_{20}$ , so that these are values which (with certain values of  $v_1$  and  $v_2$  which we will suppose fixed) satisfy (61) and (62). Then the entropy of the first body is

$$\eta_1 = \frac{R}{N} \log K_1(\epsilon_{10}, v_1), \quad . \quad . \quad . \quad (67)$$

and that of the second body

$$\eta_2 = \frac{R}{N} \log K_2(\epsilon_{20}, v_2), \quad . \quad . \quad . \quad (68)$$

and the entropy of the whole system is, according to thermodynamics, equal to the sum of these two. Is this still the case if the latter entropy is calculated according to the definition of Article 14 ?



To answer this question we have to find the region  $Kd\epsilon$  of the phase-space which corresponds to the interval  $\epsilon$  to  $\epsilon + d\epsilon$  of the total energy, keeping in mind that to this region belong also states in which the energies of the two bodies deviate from  $\epsilon_{10}$  and  $\epsilon_{20}$ .

We may start from (60b). Let in this formula  $\epsilon_1 = \epsilon_{10} + \theta$ , and therefore  $\epsilon_2 = \epsilon_{20} - \theta$ . Instead of the variable  $\epsilon_1$  we can introduce the deviation  $\theta$  and we thus find

$$G = K_{1(v_1, \epsilon_{10} + \theta)} d\theta K_{2(v_2, \epsilon_{20} - \theta)} d\epsilon. \quad (69)$$

Integrating this over all possible values of the deviation  $\theta$  we shall find the required region  $Kd\epsilon$ . Thus

$$K = \int K_{1(v_1, \epsilon_{10} + \theta)} K_{2(v_2, \epsilon_{20} - \theta)} d\theta. \quad (70)$$

We can simplify matters by assuming that perceptible deviations from  $\epsilon_{10}$  are exceedingly rare, so that  $\theta$  is very small. In the logarithm of the product  $K_1 K_2$  occurs, apart from the factor  $N/R$ , the sum of the entropies, and this sum can be developed into a Taylor series. This gives

$$\begin{aligned} \eta_{1(v_1, \epsilon_{10} + \theta)} + \eta_{2(v_2, \epsilon_{20} - \theta)} &= \eta_{10} + \theta \frac{\partial \eta_1}{\partial \epsilon_1} + \frac{1}{2} \theta^2 \frac{\partial^2 \eta_1}{\partial \epsilon_1^2} + \eta_{20} - \theta \frac{\partial \eta_2}{\partial \epsilon_2} + \frac{1}{2} \theta^2 \frac{\partial^2 \eta_2}{\partial \epsilon_2^2} \\ &= \eta_{10} + \eta_{20} + \frac{1}{2} \theta^2 \left( \frac{\partial^2 \eta_1}{\partial \epsilon_1^2} + \frac{\partial^2 \eta_2}{\partial \epsilon_2^2} \right), \end{aligned}$$

since, by (61), the two terms with the factor  $\theta$  cancel. Thus,

$$K_1 K_2 = e^R \left[ \eta_{10} + \eta_{20} + \frac{1}{2} \theta^2 \left( \frac{\partial^2 \eta_1}{\partial \epsilon_1^2} + \frac{\partial^2 \eta_2}{\partial \epsilon_2^2} \right) \right] \quad (71)$$

$$K = e^{\frac{N}{R}(\eta_{10} + \eta_{20})} \int_{-\infty}^{+\infty} e^{\frac{1}{2} \frac{N}{R} \theta^2 \left( \frac{\partial^2 \eta_1}{\partial \epsilon_1^2} + \frac{\partial^2 \eta_2}{\partial \epsilon_2^2} \right)} d\theta. \quad (72)$$

The integral can safely be extended from  $-\infty$  to  $+\infty$ , although somewhat large values of  $\theta$  do not actually occur. For such values contribute practically nothing to the integral, provided the exponent, which will presently be seen to be negative, is sufficiently large. Now, by (59),

$$\frac{\partial^2 \eta}{\partial \epsilon^2} = -\frac{1}{T^2} \left( \frac{\partial T}{\partial \epsilon} \right)_v = -\frac{1}{T^2 c_v},$$

where  $c_v$  is the specific heat at constant volume. Thus the exponent of  $e$  under the integration sign becomes

$$-\frac{N}{2RT^2} \left\{ \frac{1}{c_{v_1}} + \frac{1}{c_{v_2}} \right\} \theta^2,$$

and 
$$K = e^{\frac{N}{R}(\eta_{10} + \eta_{20})} \int_{-\infty}^{+\infty} e^{-\frac{N}{2RT^2} \left( \frac{1}{c_{v1}} + \frac{1}{c_{v2}} \right) \theta^2} d\theta. \quad (73)$$

This integral can be evaluated, and we thus find

$$K = e^{\frac{N}{R}(\eta_{10} + \eta_{20})} \sqrt{\frac{2\pi RT^2}{N} \cdot \left( \frac{1}{c_{v1}} + \frac{1}{c_{v2}} \right)^{-1}}, \quad (74)$$

whence

$$\eta = \frac{R}{N} \log K = \eta_{10} + \eta_{20} + \frac{R}{2N} \left\{ \log (2\pi) + \log \frac{R}{N} + 2 \log T - \log \left( \frac{1}{c_{v1}} + \frac{1}{c_{v2}} \right) \right\}. \quad (75)$$

Now, as we know,  $R/N = \frac{2}{3}a$  (if  $aT$  be the mean kinetic energy of a molecule). Thus  $R/N$  is quite small. The first, the third, and the fourth terms in the brackets are not large, but  $\log R/N$  is. Since, however,  $\lim_{x \rightarrow 0} x \log x = 0$ , the whole expression

$$\frac{R}{2N} \left\{ \log (2\pi) + \log \frac{R}{N} + 2 \log T - \log \left( \frac{1}{c_{v1}} + \frac{1}{c_{v2}} \right) \right\}$$

can be neglected in presence of  $\eta_{10} + \eta_{20}$ , these two terms not being small. Ultimately, therefore,

$$\eta = \eta_{10} + \eta_{20}, \quad (76)$$

wherewith our question is answered in the affirmative.

It is very remarkable that these considerations, in which account was taken of the deviations from the most probable state, lead to a result in which appear only the quantities  $\eta_{10}$  and  $\eta_{20}$  belonging to that state itself. This is due to the very large number of molecules. For thus it comes that, while  $\eta_{10}$ ,  $\eta_{20}$ , and  $R$  are by no means small,  $R/N$  is quite small.

## CHAPTER V

### CONNECTION BETWEEN THE ENTROPY AND BOLTZMANN'S FUNCTION H

#### 17. PROOF OF $\eta = -\frac{R}{N}H$

WE begin by recalling the usual definition of the function H. This is, for a monatomic gas, according to Boltzmann,\*

$$H = \int f \log f dS,$$

where  $f$  is the function which determines the distribution of the molecule points in the velocity space (co-ordinates  $\xi, \eta, \zeta$ ),  $dS = d\xi d\eta d\zeta$  represents an element of that space, and  $f dS$  is the number of points therein contained.

The same formula holds also for a gas consisting of polyatomic molecules, each having, say,  $s$  degrees of freedom, provided that  $dS$  be an element of the  $2s$ -dimensional manifold belonging to a molecule.

Now, the entropy is related to this function H by the following equation :

$$\eta = -\frac{R}{N}H. \quad . \quad . \quad . \quad . \quad . \quad (76a)$$

We will prove this statement using the definition (52) of the entropy. We thus begin by determining  $Kd\epsilon$ , viz. for the case of a gas consisting of  $n$  molecules of any structure whatever, disregarding, however, their dimensions.

We first fix our attention upon the  $2s$ -dimensional phase-space of one of the  $n$  molecules, and then compound these particular spaces into a  $2sn$ -dimensional phase-space for the whole

\* L. Boltzmann, *Vorlesungen über Gastheorie*, i., p. 32 et seq.

system. We divide the phase-space of a molecule into  $k$  equal elements  $dS$ , viz.  $dS_1, \dots, dS_k$ .

Now, suppose there are  $n_1$  assigned molecules in  $dS_1$ , similarly  $n_2$  in  $dS_2$ , etc.,  $n_k$  in  $dS_k$ .

In order to find that portion of Gibbs' phase-space which corresponds to this configuration, we have to take the product of the elements of the phase-spaces belonging to each molecule. We thus find

$$dS_1^{n_1} \dots dS_k^{n_k} = dS^n,$$

since  $dS_1 = \dots = dS_k = dS$  and  $n_1 + \dots + n_k = n$ .

Next, the portion of the phase-space which corresponds to the configuration of

$$\begin{array}{ccccccc} n_1 & \text{arbitrary} & \text{molecules in } dS_1 & & & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ n_k & \text{,,} & \text{,,} & \text{,,} & \text{,,} & dS_k & \end{array}$$

will be

$$\frac{n!}{n_1! \dots n_k!} dS^n, \quad \dots \quad (77)$$

i.e.  $\frac{n!}{n_1! \dots n_k!}$  times the preceding one, for  $n$  molecules can be

arranged into  $\frac{n!}{n_1! \dots n_k!}$  different groups of  $n_1, \dots, n_k$  molecules.

But we have still to take account of the  $\epsilon$ -condition, i.e. to retain only those items ( $n_1, \dots, n_k$ ) for which the energy lies between  $\epsilon$  and  $\epsilon + d\epsilon$ . Thus we have

$$Kd\epsilon = \sum \frac{n!}{n_1! \dots n_k!} dS^n, \quad \dots \quad (78)$$

where the sum is to be extended over all combinations  $n_1, \dots, n_k$  satisfying this energy condition.

In order to bring all this into connection with H we must keep in mind that in the formula for H occurs only the actual or, as we may say, the most probable distribution of states, while in (78) the sum has to be extended over different distributions within the interval determined by  $d\epsilon$ . Suppose that, with the given  $\epsilon$ , the expression

$$\frac{n!}{n_1! \dots n_k!} \quad \dots \quad (79)$$

attains a maximum for the values  $n_{10} \dots n_{k0}$ . What will be the value of this expression for values of  $n_1 \dots n_k$  differing somewhat from  $n_{10} \dots n_{k0}$ , say for

$$n_1 = n_{10} + \nu_1, \dots, n_k = n_{k0} + \nu_k,$$

where the  $\nu$ 's are positive or negative integers small compared with  $n_{10} \dots n_{k0}$ , and  $\nu_1 + \dots + \nu_k = 0$ ?

If  $n_{10} \dots n_{k0}$  are replaced by  $n_{10} + \nu_1 \dots n_{k0} + \nu_k$ , the denominator of (79) becomes somewhat greater. This increase can be calculated by means of Stirling's formula  $n_1! = n_1^{n_1 + \frac{1}{2}} \sqrt{2\pi} e^{-n_1}$ , for very great  $n_1$ . This gives

$$n_1! \dots n_k! = n_1^{n_1 + \frac{1}{2}} \dots n_k^{n_k + \frac{1}{2}} (2\pi)^{\frac{1}{2}k} e^{-n}, \quad (80)$$

whence

$$g \equiv \frac{(n_{10} + \nu_1)! \dots (n_{k0} + \nu_k)!}{n_{10}! \dots n_{k0}!} = \frac{(n_{10} + \nu_1)^{n_{10} + \nu_1 + \frac{1}{2}} \dots (n_{k0} + \nu_k)^{n_{k0} + \nu_k + \frac{1}{2}}}{n_{10}^{n_{10} + \frac{1}{2}} \dots n_{k0}^{n_{k0} + \frac{1}{2}}}; \quad (81)$$

this is the factor by which the denominator of (79) has to be multiplied in order to find the effect of the  $\nu$ 's.

Now,

$$\log g = (n_{10} + \nu_1 + \frac{1}{2}) \left\{ \log n_{10} + \log \left( 1 + \frac{\nu_1}{n_{10}} \right) \right\} + \dots - (n_{10} + \frac{1}{2}) \log n_{10} - \dots, \quad (82)$$

and since  $\nu_1/n_{10}$  is very small, we have, by Taylor's theorem,

$$\log \left( 1 + \frac{\nu_1}{n_{10}} \right) = \frac{\nu_1}{n_{10}} - \frac{\nu_1^2}{2n_{10}^2}, \text{ and, remembering that } \nu_1 + \dots + \nu_k = 0,$$

$$\log g = \sum_{\lambda=1}^{\lambda=k} \left\{ \nu_\lambda \log n_{\lambda 0} + \frac{\nu_\lambda}{2n_{\lambda 0}} + \frac{\nu_\lambda^2}{2n_{\lambda 0}} - \frac{\nu_\lambda^2}{4n_{\lambda 0}^2} \right\}, \quad (83)$$

where the last bracketed term can be neglected in the presence of the remaining ones.

It will be readily seen that  $g > 1$ , so that  $\log g$  is positive.

Let  $A$  be the maximum value of (77). Then, since all values of  $n_1 \dots n_k$  occurring in the interval  $d\epsilon$  differ very little from  $n_{10} \dots n_{k0}$ , we can apply the above result and we find, by (78),

$$Kd\epsilon = \sum A \frac{1}{g} = \sum A e^{-\log g} = A \sum e^{-\log g}, \quad (85)$$

where the sum is to be extended over all combinations of  $\nu_1 \dots \nu$

compatible with  $\nu_1 + \dots + \nu_k = 0$  and with the given limits of  $\epsilon_k$  so that  $\nu_1\epsilon_1 + \dots + \nu_k\epsilon_k$  lies between 0 and  $d\epsilon$ .

Evidently, this sum can be supposed to be proportional to the interval  $d\epsilon$ , say

$$\sum e^{-\log g} = \gamma d\epsilon,$$

where  $\gamma$  is independent of  $d\epsilon$ . Thus

$$K = A\gamma$$

or

$$\log K = \log A + \log \gamma,$$

and therefore, by (52),

$$\eta = \frac{R}{N} (\log A + \log \gamma). \quad (86)$$

The long and tedious calculation of  $\gamma$  need not detain us here. It appears that the second term in (86) can be neglected in the presence of the first, so that the value of  $\eta$  depends on the distribution in the state of equilibrium. Thus the suffixes 0 can henceforth be omitted and we can write

$$A = \frac{n!}{n_1! \dots n_k!} dS^n.$$

Now, to find the relation between  $\eta$  and  $H$  we again apply Stirling's formula. This gives

$$\begin{aligned} \log A = & (n + \tfrac{1}{2}) \log n - n + \tfrac{1}{2} \log (2\pi) - \sum_{\lambda=1}^{\lambda=k} \{ (n_\lambda + \tfrac{1}{2}) \log n_\lambda \\ & - n_\lambda + \tfrac{1}{2} \log (2\pi) \} + n \log dS = (n + \tfrac{1}{2}) \log n \\ & - \sum_{\lambda=1}^{\lambda=k} \{ (n_\lambda + \tfrac{1}{2}) \log n_\lambda \} - \tfrac{1}{2} (k-1) \log (2\pi) + n \log dS. \end{aligned} \quad (87)$$

Ultimately, after some obvious omissions (in the expression for the entropy constant terms can be left out) we find

$$\eta = - \frac{R}{N} \sum_{\lambda=1}^{\lambda=k} n_\lambda \log \left( \frac{n_\lambda}{dS_\lambda} \right), \quad (88)$$

and putting  $n_\lambda = f_\lambda dS_\lambda$ , where  $f_\lambda$  is the distribution function,

$$\eta = - \frac{R}{N} \sum f_\lambda \log f_\lambda dS_\lambda = - \frac{R}{N} \int f \log f dS = - \frac{R}{N} H. \quad (89)$$

This proves the simple relation (76a) between the entropy and Boltzmann's function  $H$ .



## CHAPTER VI

APPLICATION OF THE STATISTICAL DEFINITION OF ENTROPY TO  
SPECIAL CASES

## 18. VAN DER WAALS' EQUATION OF STATE

To give an application of our definition of entropy, viz.  $\eta = R N \log K$ , we will now derive van der Waals' equation of state. A long time ago the physicists asked themselves how large they had to imagine the spheres of action of the molecules, when interacting with each other. Are they, for instance, large compared with the dimensions of the molecules themselves, so that they can be considered as spaces uniformly filled with substance? Laplace and van der Waals have formed such an idea, but, as is known in our days, this cannot be correct (apparent association). Yet, to arrive at van der Waals' equation, we will here adopt this standpoint.

Let us then suppose a volume  $v$  to contain  $n$  molecules of a certain finite extension, which attract each other and possess a total energy ranging from  $\epsilon$  to  $\epsilon + d\epsilon$ . In view of the existence of mutual molecular attraction (van der Waals'  $a$ ) this energy has to be thought of as partly *kinetic* and partly *potential*.

The potential energy can be expressed by

$$-\frac{kn^2}{2v},$$

where  $k$  is a constant.

We assume that the molecules are uniformly distributed over the volume and that the potential energy vanishes when they are very far apart.

Put  $\epsilon + \frac{kn^2}{2\eta} = \epsilon'$ , . . . . . (90)

so that, the value of the potential energy being fixed, that of the kinetic energy is contained between  $\epsilon'$  and  $\epsilon' + d\epsilon$ . Turning now to Gibbs' phase-space, we have to integrate over the co-ordinates and the momenta of all molecules. In the present case the two integrations can be strictly separated.

If the molecules occupied no space, the integration over the co-ordinates would, by (53a), give  $v^n$ .

Taking their extension into account we can write instead

$$(\omega v)^n, \quad . \quad . \quad . \quad . \quad . \quad (90a)$$

where  $\omega$  is a function of

$$\nu = \frac{n}{v} \quad . \quad . \quad . \quad . \quad . \quad (90b)$$

the number of molecules per unit volume.

The integration over the momenta gives

$$\frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n)} \epsilon'^{\frac{3}{2}n-1} d\epsilon; \quad . \quad . \quad . \quad . \quad (90c)$$

this is based on formula (55) where we have substituted

$$\Gamma(\frac{3}{2}n + 1) = \frac{3}{2}n \Gamma(\frac{3}{2}n).$$

Thus, 
$$K d\epsilon = (\omega v)^n \frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n)} \epsilon'^{\frac{3}{2}n-1} d\epsilon, \quad . \quad . \quad . \quad (91)$$

the required expression for  $K$  and thus also for  $\eta$ .

These considerations and formulæ resemble very much those of page 178 *et seq.* There, however, we have considered a gas without molecular attraction and finite extension of the molecules, *i.e.* without van der Waals'  $a$  and  $b$ , while here we just consider a gas such as treated by van der Waals. Hence the appearance of the factor  $\omega^n$  in the expression for the energy.

Substituting (90) in (91), one finds

$$K = (\omega v)^n \frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n)} \left( \epsilon + \frac{kn^2}{2v} \right)^{\frac{3}{2}n-1} \quad . \quad . \quad . \quad (92)$$

and therefore,

$$\eta = \frac{R}{N} \left\{ \frac{3}{2}n \log (2\pi m) - \log \Gamma(\frac{3}{2}n) + n \log (\omega v) + (\frac{3}{2}n - 1) \log \left( \epsilon + \frac{kn^2}{2v} \right) \right\}. \quad (93)$$

As we know, the relations

$$\frac{\partial \eta}{\partial \epsilon} = \frac{1}{T} \quad \text{and} \quad \frac{\partial \eta}{\partial v} = \frac{p}{T}$$

must hold also for the entropy derived in this way. The equation of state will, therefore, be obtained by differentiating the last expression for  $\eta$  with respect to  $\epsilon$  and  $v$ . Thus we find, in the first place,

$$\frac{\partial \eta}{\partial \epsilon} = \frac{1}{T} = \frac{R}{N} \frac{\frac{3}{2}n}{\epsilon + \frac{kn^2}{2v}} \text{ or } \epsilon + \frac{kn^2}{2v} = \frac{R}{N} \cdot \frac{3}{2}nT. \quad (94)$$

This equation tells us that the mean kinetic energy of a molecule has a determined value which is proportional to  $T$ . Since  $\frac{3}{2} \frac{R}{N} = \alpha$ , we may also write

$$\epsilon + \frac{kn^2}{2v} = n\alpha T. \quad (95)$$

In the second place, differentiating with respect to  $v$  we have to keep in mind that  $\omega$  also depends on  $v$ . We introduce the quantity  $\nu$ , by (90b),

$$\nu = \frac{n}{v}; \quad d\nu = -\frac{n}{v^2}dv = -\frac{\nu}{v}dv;$$

thus, 
$$\frac{\partial \omega}{\partial v} = -\frac{\nu}{v} \frac{\partial \omega}{\partial \nu}.$$

The differentiation now gives

$$\begin{aligned} \frac{\partial}{\partial v} \{n \log(\omega v)\} &= \frac{n}{\omega v} \left( v \frac{\partial \omega}{\partial v} + \omega \right) \\ &= \frac{n}{\omega} \frac{\partial \omega}{\partial v} + \frac{n}{v} = -\frac{\nu}{v} \frac{n}{\omega} \frac{\partial \omega}{\partial \nu} + \nu = -\frac{\nu^2}{\omega} \frac{\partial \omega}{\partial \nu} + \nu, \end{aligned}$$

so that ultimately we find

$$\frac{\partial \eta}{\partial v} = \frac{p}{T} = \frac{R}{N} \left\{ \nu - \frac{\nu^2}{\omega} \frac{d\omega}{d\nu} - \frac{3}{2}n \frac{kn^2/2v^2}{\epsilon + kn^2/2v} \right\} \quad (96)$$

or, by (94),

$$\frac{p}{T} = \frac{R}{N} \left\{ \nu - \frac{\nu^2}{\omega} \frac{d\omega}{d\nu} \right\} - \frac{1}{T} \frac{kn^2}{2v^2}. \quad (97)$$

*This is the equation of state* which, to make its analogy with that of van der Waals more evident, can also be written in the form

$$p + \frac{kn^2}{2v^2} = \frac{RT}{N} \left\{ \nu - \frac{\nu^2}{\omega} \frac{d\omega}{d\nu} \right\}. \quad (98)$$

What can still be said about the quantity  $\omega$ ? The integration over the co-ordinates of the centres of all molecules without

extension would, by (53a), give  $v^n$ . If we ascribe to the molecules a finite extension, we find for the first molecule again  $v$ , but for the second one a little less than this, since by the presence of the first molecule the space available for the second molecule is reduced, viz. to  $v$  times a number smaller than 1; for the third molecule the result is still somewhat smaller, and so on. Suppose we find for the last molecule  $\kappa v$ ; then  $\kappa$  can depend only on the density. Thus we see that  $\omega$  is a function of  $\nu$ , the number of molecules per unit volume; with increasing  $\nu$ , i.e. with increasing density,  $\omega$  becomes smaller. The derivative  $d\omega/d\nu$  is, therefore, negative and the last term in (98) has the tendency of increasing the pressure, as was to be expected.

It is indeed a matter of regret that even for spherical molecules  $\omega$  cannot be calculated rigorously as a function of  $\nu$ . One has to help himself with approximate assumptions, as *e.g.* that the extension of the molecules is small compared with the volume  $v$ . In some such way one can ultimately reduce the equation to van der Waals' form.

#### 19. EQUILIBRIUM BETWEEN COEXISTING PHASES\* OF A VAN DER WAALSIA SUBSTANCE, TREATED BY GIBBS' METHOD

We will now turn to consider the equilibrium between two coexisting phases, *e.g.* a liquid and vapour, of a substance of the van der Waals type.

The two phases will be referred to as (1) and (2), and the quantities associated with them will be marked by the suffixes 1 and 2. Let the total volume of both phases be  $v$ , and let the total energy be contained between  $\epsilon$  and  $\epsilon + d\epsilon$ . To begin with, we consider the following state:

phase (1):  $n_1$  assigned molecules, volume  $= v_1$ , energy between  $\epsilon_1$  and  $\epsilon_1 + d\epsilon_1$ ,

phase (2):  $n_2$  assigned molecules, volume  $= v_2$ , energy between  $\epsilon_2$  and  $\epsilon_2 + d\epsilon_2$ ,

where  $v_1 + v_2 = v$  and  $\epsilon_1 + \epsilon_2 = \epsilon$ .

Taking the phase (1) first, we can apply to it all that has been said above about a homogeneous substance. In fact, this phase

\* The term "phases" is here used in the ordinary thermodynamical sense. That this word is used now in the thermodynamical and now in Gibbs' sense, will scarcely give rise to a misunderstanding.

considered by itself is nothing else than a certain amount of a homogeneous substance. Thus, by (93),

$$\eta_1 = \frac{R}{N} \left[ \frac{3}{2} n_1 \log (2\pi m) - \log \Gamma\left(\frac{3}{2} n_1\right) + n_1 \log (\omega_1 v_1) + \frac{3}{2} n_1 \log \left( \epsilon_1 + \frac{k n_1^2}{2 v_1} \right) \right]. \quad (99)$$

The portion of the representative space for phase (1), which corresponds to  $v_1$ ,  $\epsilon_1$ , and  $d\epsilon_1$ , is, as we know [cf. (52)],

$$K_1 d\epsilon_1 = e^{\frac{N}{R} \eta_1} d\epsilon_1,$$

and similarly for phase (2)

$$K_2 d\epsilon_2 = e^{\frac{N}{R} \eta_2} d\epsilon_2.$$

Hence the portion of the compound phase-space belonging to our whole system

$$e^{\frac{N}{R} (\eta_1 + \eta_2)} d\epsilon_1 d\epsilon_2. \quad . \quad . \quad . \quad . \quad (100)$$

We have assumed, however, that the phase (1) is formed of  $n_1$  *assigned* molecules, and similarly for the phase (2), while for the equilibrium it is actually irrelevant *which* molecules these are. The last expression has, therefore, still to be multiplied by the number of ways in which the phases can be formed of the available

molecules. This number is  $\frac{n!}{n_1! n_2!}$ , so that the expression (100) must be replaced by

$$\frac{n!}{n_1! n_2!} e^{\frac{N}{R} (\eta_1 + \eta_2)} d\epsilon_1 d\epsilon_2. \quad . \quad . \quad . \quad (101)$$

Here  $d\epsilon_1 d\epsilon_2$  has been written instead of  $d\epsilon_1 d\epsilon_2$ , and the expression as it stands represents now that portion of the phase-space in which, with the volumes  $v_1$  and  $v_2$ , the total energy is contained between  $\epsilon$  and  $\epsilon + d\epsilon$  and that of the first phase between  $\epsilon_1$  and  $\epsilon_1 + d\epsilon_1$ . The total volume and the total energy being given,  $v_1$  and  $\epsilon_1$  can still assume different values, but the factor of  $d\epsilon_1 d\epsilon_2$  attains for certain values of  $v_1$  and  $\epsilon_1$  a maximum and, as is always the case in questions of this kind, a *very sharp* one, so that the probability of any noteworthy deviations from these values

is very small. We write, therefore, as the condition of equilibrium,

$$\frac{1}{n_1! n_2!} e^{R(\eta_1 + \eta_2)} = \max. \quad (102)$$

or also 
$$\log \frac{1}{n_1! n_2!} e^{\frac{R}{N}(\eta_1 + \eta_2)} = \max.$$

Applying again Stirling's formula to the factorials, we find, after some obvious omissions, the condition

$$\eta_1 - \frac{R}{N} n_1 \log n_1 + \eta_2 - \frac{R}{N} n_2 \log n_2 = \max. \quad (103)$$

The terms containing the logarithms can by no means be cancelled and are just necessary to obtain a result which is in good agreement with thermodynamics. For  $\eta_1$  (and similarly for  $\eta_2$ ) the long formula (99) has to be used. We can put

$$\Gamma(\frac{3}{2}n_1) = (\frac{3}{2}n_1)^{\frac{3}{2}n_1}, \quad (104)$$

so that

$$\eta_1 - \frac{R}{N} n_1 \log n_1 = \frac{R}{N} \left\{ \frac{3}{2} n_1 \log (2\pi m) + n_1 \log \frac{\omega_1 v_1}{n_1} - \frac{3}{2} n_1 \log \left( \frac{3}{2} \right) + \frac{3}{2} n_1 \log \left( \frac{\epsilon_1}{n_1} + \frac{n_1}{2} \frac{k}{v_1} \right) \right\}. \quad (105)$$

We have written the equation in this form in order to bring it into evidence that at a given density and temperature of the first phase the second member is proportional to the quantity of this phase. In fact, each term contains  $n_1$  as factor, and when the quantity of the phase is varied,  $v_1$  and  $\epsilon_1$  vary proportionally to  $n_1$ , while  $\omega_1$  remains unaltered. Thus, if the first phase contains  $a_1$  gram molecules, the expression  $\eta_1 - \frac{R}{N} n_1 \log n_1$  is  $a_1$  times that for one gram molecule (and for the latter a formula of the same form as (105) can be written), so that, if  $\eta_1$  be the entropy of a gram molecule in phase (1),

$$\eta_1 - \frac{R}{N} n_1 \log n_1 = a_1(\bar{\eta}_1 - R \log N).$$

Similarly, if there are  $a_2$  gram molecules in the phase (2) and if  $\eta_2$  be the entropy of this phase per gram molecule,

$$\eta_2 - \frac{R}{N} n_2 \log n_2 = a_2(\eta_2 - R \log N).$$



Substituting these values in (103) and remembering that  $a_1 + a_2$  is constant we obtain the condition

$$\overline{a_1\eta_1} + \overline{a_2\eta_2} = \max., \quad . \quad . \quad . \quad (109)$$

which solves the problem.

In fact, from (109) it is easy to deduce the known equilibrium conditions, viz. the equality of temperature ( $T$ ), pressure ( $p$ ), and the thermodynamical potential per gram molecule ( $\zeta = \epsilon - T\eta + pv$ ) of the two phases. We retain the suffixes 1 and 2, but write henceforth  $\eta_1, \eta_2$  instead of  $\overline{\eta_1}, \overline{\eta_2}$ . Thus the equilibrium condition becomes

$$a_1\eta_1 + a_2\eta_2 = \max.,$$

the variations of  $a_1, a_2, v_1, v_2, \epsilon_1, \epsilon_2$  being subjected to the conditions

$$a_1 + a_2 = \text{const.}$$

$$a_1v_1 + a_2v_2 = \text{const.}$$

$$a_1\epsilon_1 + a_2\epsilon_2 = \text{const.}$$

Taking the variations of these equations, multiplying three of them by constant factors, adding up and equating to zero the coefficients of  $\delta a_1$ , etc., we find

$$\frac{\partial \eta_1}{\partial \epsilon_1} = \frac{\partial \eta_2}{\partial \epsilon_2} \quad \text{or} \quad T_1 = T_2, \quad . \quad . \quad . \quad (111)$$

$$\frac{\partial \eta_1}{\partial v_1} = \frac{\partial \eta_2}{\partial v_2}, \quad \text{or} \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}, \quad \therefore p_1 = p_2, \quad . \quad . \quad (112)$$

and, finally,

$$\eta_1 - \frac{\epsilon_1}{T_1} - \frac{p_1v_1}{T_1} = \eta_2 - \frac{\epsilon_2}{T_2} - \frac{p_2v_2}{T_2},$$

$$\text{or} \quad \epsilon_1 - \eta_1T_1 + p_1v_1 = \epsilon_2 - \eta_2T_2 + p_2v_2, \quad i.e. \quad \zeta_1 = \zeta_2. \quad . \quad (113)$$

## 20. A VAN DER WAALSIA SUBSTANCE UNDER CONSERVATIVE EXTERNAL FORCES, TREATED BY GIBBS' METHOD

We will now consider a substance of the van der Waals type subjected to external forces, under whose action the state is not throughout the same. We assume that the forces are conservative, so that a potential exists.

Let  $\chi$ , a function of the co-ordinates, be the potential energy

per molecule, and let the energy of the whole system lie between  $\epsilon$  and  $\epsilon + d\epsilon$ .

The portion of Gibbs' phase-space belonging to our system is  $Kd\epsilon$ , and the problem consists in finding  $K$ .

We divide the space occupied by the substance into volume-elements  $dS_1 \dots dS_k$ .

To begin with, we suppose that there are  $n_1$  molecules in  $dS_1$ ,  $n_2$  molecules in  $dS_2$ , etc., and, as we have repeatedly done, we split the phase-space into two parts, one for the momenta and one for the co-ordinates, and we choose  $n_1$  *assigned* molecules for  $dS_1$ , etc. The integration over the co-ordinates is then easily accomplished and gives for the first group of molecules  $(\omega_1 dS_1)^{n_1}$ , for the second  $(\omega_2 dS_2)^{n_2}$ , etc., where  $\omega_1 \dots$  are again the same functions of the density as before. Cf. (90b). This gives for the total co-ordinate space corresponding to  $n_1$  assigned molecules in  $dS_1$ ,  $n_2$  in  $dS_2$ , etc.

$$(\omega_1 dS_1)^{n_1} \dots (\omega_k dS_k)^{n_k} \dots \quad (114)$$

This expression is analogous to (90a), apart from the circumstance that, owing to the external forces, the density of the distribution of the molecules over the space varies from point to point, so that the  $\omega$ 's can no longer be considered as constant.

Passing now to  $n_1$  *arbitrary* molecules in  $dS_1$ , etc., we have again (as on p. 193) to multiply the last expression by the number of ways in which the available molecules can be arranged into groups of  $n_1, n_2$ , etc. This number is

$$\frac{n!}{n_1! \dots n_k!},$$

so that instead of (114) we have

$$\frac{n!}{n_1! \dots n_k!} (\omega_1 dS_1)^{n_1} \dots (\omega_k dS_k)^{n_k} \dots \quad (115)$$

The potential energy of the external forces is

$$n_1 \chi_1 + \dots + n_k \chi_k. \quad (116)$$

If we assume that the capillary forces within the substance can be disregarded, the potential energy of van der Waals' molecular attraction is, in each element, determined by the density and can thus be written

$$-\frac{1}{2}k \left( \frac{n_1^2}{dS_1} + \dots + \frac{n_k^2}{dS_k} \right); \quad (117)$$

so that the total potential energy becomes

$$n_1\chi_1 + \dots + n_k\chi_k - \frac{1}{2}k\left(\frac{n_1^2}{dS_1} + \dots + \frac{n_k^2}{dS_k}\right). \quad (118)$$

We now write again

$$\epsilon' = \epsilon - (n_1\chi_1 + \dots) + \frac{1}{2}k\left(\frac{n_1^2}{dS_1} + \dots\right), \quad (119)$$

where  $\epsilon$  is the total and  $\epsilon'$  the kinetic energy.

The kinetic energy of the whole system must thus be contained between  $\epsilon'$  and  $\epsilon' + d\epsilon$ , and this determines the intervals for the velocities or the momenta of the molecules. Similarly as before [cf. (90c)] we find for the portion of the space of momenta

$$\frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n)} \epsilon'^{\frac{3}{2}n-1} d\epsilon, \quad (120)$$

and since  $Kd\epsilon$  is the product of (115) into (120), we have

$$K = \frac{(2\pi m)^{\frac{3}{2}n}}{\Gamma(\frac{3}{2}n)} \frac{n!}{n_1! \dots n_k!} (\omega_1 dS_1)^{n_1} \dots (\omega_k dS_k)^{n_k} \epsilon'^{\frac{3}{2}n}. \quad (121)$$

What is now the necessary condition that,  $\epsilon$  being given,  $K$  or  $\log K$  shall be a maximum?

Applying Stirling's formula and condensing all constant terms in  $C$ , we have

$$\log K = L = n_1 \log \frac{\omega_1 dS_1}{n_1} + \dots + n_k \log \frac{\omega_k dS_k}{n_k} + \frac{3}{2}n \log \epsilon' + C. \quad (122)$$

The conditions for  $L = \text{maximum}$  are readily found to be

$$\frac{\partial L}{\partial n_1} = \frac{\partial L}{\partial n_2} = \dots = \frac{\partial L}{\partial n_k},$$

or 
$$\frac{\partial L}{\partial n_\lambda} = C_1, \quad (123)$$

where  $\lambda$  is any of the suffixes. Keeping  $\epsilon$  constant and substituting (119) in (122), we have

$$\frac{\partial L}{\partial n_\lambda} = \log \frac{\omega_\lambda dS_\lambda}{n_\lambda} + n_\lambda \frac{1}{\omega_\lambda} \frac{d\omega_\lambda}{dn_\lambda} - 1 + \frac{3}{2}\epsilon' \left( k \frac{n_\lambda}{dS_\lambda} - \chi_\lambda \right) = C_1. \quad (124)$$

With  $\nu_\lambda = \frac{n_\lambda}{dS_\lambda}$  (density of molecules in  $dS_\lambda$ ), and omitting the subscript  $\lambda$  of  $\nu$ ,  $\omega$ ,  $\chi$ , the last condition becomes

$$\log \frac{\omega}{\nu} + \frac{\nu}{\omega} \frac{d\omega}{d\nu} - \frac{3n}{2\epsilon'} \chi + \frac{3n}{2\epsilon'} h\nu = C_2 \quad (125)$$

In this equation  $n$  is the total number of molecules and  $\epsilon'$  the total kinetic energy, while  $\nu$ ,  $\omega$ , and  $\chi$  are local values.

In order to see whether this result is in agreement with the more familiar theories, we will now try to deduce from it a known equilibrium condition.

Let us suppose for the sake of simplicity that  $\chi$  depends only on the co-ordinate  $z$ . (The general case can be treated in a similar way.)

We substitute for  $\epsilon'$  in (125) the expression

$$\epsilon' = \frac{3}{2} n \frac{RT}{N}, \quad (126)$$

where  $N$  is the number of molecules per gram molecule, and differentiate with respect to  $z$ , keeping in mind that  $\omega$  is a function of  $\nu$ . This gives

$$\left\{ \frac{2\nu}{\omega} \frac{d\omega}{d\nu} - \frac{\nu^2}{\omega^2} \left( \frac{d\omega}{d\nu} \right)^2 - 1 + \frac{\nu^2}{\omega} \frac{d^2\omega}{d\nu^2} + \frac{N}{RT} k\nu \right\} \frac{d\nu}{dz} - \frac{N}{RT} \nu \frac{d\chi}{dz} = 0. \quad (127)$$

We have found before [cf. (97)]

$$p \frac{N}{RT} = \nu - \frac{\nu^2}{\omega} \frac{d\omega}{d\nu} - \frac{1}{2} k \nu^2 \frac{N}{RT}, \quad (128)$$

which, differentiated with respect to  $z$ , gives

$$\frac{N}{RT} \frac{dp}{dz} = \left\{ 1 - \frac{2\nu}{\omega} \frac{d\omega}{d\nu} + \frac{\nu^2}{\omega^2} \left( \frac{d\omega}{d\nu} \right)^2 - \frac{\nu^2}{\omega} \frac{d^2\omega}{d\nu^2} - \frac{N}{RT} k\nu \right\} \frac{d\nu}{dz}. \quad (129)$$

Combining (129) with (127) we find

$$\frac{dp}{dz} + \nu \frac{d\chi}{dz} = 0, \quad (130)$$

and this is the well-known equation which says that the action of the external forces upon a given volume-element is balanced by the pressure exerted upon that element by the surrounding volume-elements.

## 21. THE SAME PROBLEM TREATED BY BOLTZMANN'S H-THEOREM

It has already been mentioned that all such results can also be derived by means of Boltzmann's  $H$ -theorem. In fact, we have proved that Gibbs' and Boltzmann's methods are essentially equivalent to each other.

We will now apply the  $H$ -theorem to the case treated above.

For the  $H$ -function of a gas consisting of molecules of finite dimensions Ornstein \* finds

$$H = \int f \log \frac{f}{\omega} dS d\lambda, \quad . \quad . \quad . \quad (131)$$

where  $dS$  is an ordinary space element,  $d\lambda$  an element of the velocity space, and thus  $dS d\lambda$  an element of the six-dimensional manifold which contains  $f dS d\lambda$  molecules, while  $\omega$  is the function of density introduced before. If we now require that, for a given volume and total energy,  $H$  should be as small as possible, we shall arrive again at the previous result. And since  $f$  indicates also the distribution of the molecule-points in the space of velocities, we should by determining  $f$  find at the same time Maxwell's law and the distribution of molecules over the volume of the gas. We denote by  $x, y, z$  the co-ordinates and by  $\xi, \eta, \zeta$  the velocity components, and assume that the number of elements  $dS$  and  $d\lambda$  is very large but finite. Let these numbers be  $k$  and  $s$  respectively. Any elements of the two spaces will be denoted by  $dS_\kappa$  and  $d\lambda_\sigma$ .

Thus  $H$  can be written

$$H = \sum_{\kappa\sigma} f_{\kappa\sigma} \log \frac{f_{\kappa\sigma}}{\omega_{\kappa}} dS_\kappa d\lambda_\sigma, \quad . \quad . \quad . \quad (132)$$

where the sum is to be extended over all values 1 to  $k$  of  $\kappa$  and all values 1 to  $s$  of  $\sigma$ . This expression has to be made a minimum.

Let us first see what we can learn from (132) about the distribution of velocities. For this purpose we assume a given distribution of the molecules in space and ask what the distribution of velocities must be in order that  $H$  shall be a minimum.

Thus, let there be  $n_\kappa$  molecules in  $dS_\kappa$ . This gives as supplementary conditions, one for each value of  $\kappa$ ,

$$\sum_{\sigma} f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = n_\kappa. \quad . \quad . \quad . \quad (133)$$

In addition to this we have still to take account of the energy condition, which amounts to requiring that the kinetic energy

$$\sum_{\kappa\sigma} f_{\kappa\sigma} \frac{1}{2} m (\xi_\sigma^2 + \eta_\sigma^2 + \zeta_\sigma^2) dS_\kappa d\lambda_\sigma = \epsilon' \quad . \quad . \quad (134)$$

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\* L. S. Ornstein, *Dissertation*, Leiden, 1908, pp. 59 and 60, or *Arch. néerl.* (3), vol. iv., p. 238, 1918.

should have a given value. In fact, the potential energy is already fixed by the choice of the space distribution.

The problem now consists in so determining  $f$  as to make  $H$  a minimum and to satisfy the conditions (133) and (134). This is an ordinary problem in variations.

Noting that, by (133) and since  $\omega_\kappa$  is fixed through the choice of the space distribution,

$$\sum_{\kappa\sigma} f_{\kappa\sigma} \log \omega_\kappa dS_\kappa d\lambda_\sigma = \sum_{\kappa} \log \omega_\kappa \sum_{\sigma} f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = \text{constant}, \quad (135)$$

and that 
$$\sum_{\kappa\sigma} \delta f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = 0, \quad . \quad . \quad . \quad (136)$$

we find for the minimum condition of  $H$  the simple relation

$$\sum_{\kappa\sigma} \log f_{\kappa\sigma} \delta f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = 0 \quad . \quad . \quad . \quad (137)$$

with the supplementary conditions

$$\sum_{\sigma} \delta f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = 0 \quad (k \text{ equations}) \quad . \quad . \quad . \quad (138)$$

and, by (134),

$$\sum_{\kappa\sigma} \delta f_{\kappa\sigma} \cdot \frac{1}{2} m r_{\sigma}^2 dS_\kappa d\lambda_\sigma = 0 \quad (\text{one equation}), \quad . \quad . \quad (139)$$

where  $r_{\sigma}^2 = \xi_{\sigma}^2 + \eta_{\sigma}^2 + \zeta_{\sigma}^2$ .

This gives for  $f_{\kappa\sigma}$  after a few reductions, which for brevity may be here omitted, the value

$$f_{\kappa\sigma} = \delta_\kappa e^{-\frac{1}{2} m h r_{\sigma}^2}, \quad . \quad . \quad . \quad (140)$$

where the coefficients  $\delta_\kappa$  are different for different elements  $dS_\kappa$ , and  $h$  is a constant common to all elements. This result is nothing else than *Maxwell's law*.

The mean kinetic energy of a molecule is  $3/2h$ , so that

$$\epsilon' = \frac{3n}{2h} \quad . \quad . \quad . \quad (141)$$

Multiplying (140) by  $d\lambda_\sigma$  and integrating over all elements  $d\lambda$ , we shall find, of course, the density of molecules in  $dS_\kappa$ , *i.e.*  $n_\kappa/dS_\kappa$ . Now, since in this integration  $\delta_\kappa$  remains constant,

$$\int_{-\infty}^{+\infty} f_{\kappa\sigma} d\lambda = \delta_\kappa \int_{-\infty}^{+\infty} e^{-\frac{1}{2} m h r_{\sigma}^2} d\lambda = \delta_\kappa \left[ \int_{-\infty}^{+\infty} e^{-\frac{1}{2} m h \xi_{\sigma}^2} d\xi \right]^3 = \delta_\kappa \left( \frac{2\pi}{mh} \right)^{\frac{3}{2}},$$

and therefore, in conjunction with (141),

$$n_\kappa = \delta_\kappa \left( \frac{2\pi}{mh} \right)^{\frac{3}{2}} dS_\kappa = \delta_\kappa \left( \frac{4\pi}{3mn} \epsilon' \right)^{\frac{3}{2}} dS_\kappa. \quad . \quad . \quad (142)$$



It remains still to find how the molecules are distributed over the volume elements  $dS_\kappa$ . This amounts to determining the values of  $n_\kappa$  and  $\delta_\kappa$  for which  $H$  becomes a minimum.

Now, substituting in (132), in accordance with (140),

$$\log f_{\kappa\sigma} = \log \delta_\kappa - \frac{1}{2} m h r^2_\sigma \quad . \quad . \quad . \quad (143)$$

and noting that

$$\sum_\sigma f_{\kappa\sigma} dS_\kappa d\lambda_\sigma = n_\kappa$$

and

$$\sum_{\kappa\sigma} f_{\kappa\sigma} \cdot \frac{1}{2} m h r^2_\sigma dS_\kappa d\lambda_\sigma = \epsilon',$$

we have

$$H = \sum_\kappa n_\kappa \log \frac{\delta_\kappa}{\omega_\kappa} - h \epsilon'. \quad . \quad . \quad . \quad (144)$$

Introducing here the value of  $\delta_\kappa$  which follows from (142) we find

$$\begin{aligned} H &= \sum_\kappa n_\kappa \log \frac{n_\kappa}{\omega_\kappa dS_\kappa} - \sum_\kappa n_\kappa \log \left( \frac{4\pi}{3mn} \epsilon' \right)^{\frac{3}{2}} - h \epsilon' \\ &= \sum_\kappa n_\kappa \log \frac{n_\kappa}{\omega_\kappa dS_\kappa} - \frac{3}{2} n \log \epsilon' - \frac{3}{2} n \log \left( \frac{4\pi}{3mn} \right) - \frac{3}{2} n. \end{aligned} \quad (145)$$

The last two terms are independent of the distribution of the molecules, so that with a view to the minimum the first two terms only have to be considered.

Thus we see that (145) says exactly the same thing as (122), where the expression which had to be made a maximum was

$$n_1 \log \frac{\omega_1 dS_1}{n_1} + \dots + n_k \log \frac{\omega_k dS_k}{n_k} + \frac{3}{2} n \log \epsilon',$$

and that result was arrived at by requiring the entropy to be a maximum.

We have now found that the same expression with the opposite sign has to be a *minimum*. We thus see that the result obtained by means of the  $H$ -theorem agrees completely with the previous one.

## 22. EQUILIBRIUM BETWEEN COEXISTING PHASES OF A VAN DER WAALSIA SUBSTANCE, TREATED BY BOLTZMANN'S $H$ -THEOREM

In conclusion we will still treat the problem of the equilibrium between two coexisting homogeneous phases by means of Boltzmann's  $H$ -theorem.

We consider a vessel containing a van der Waalsian substance consisting of  $n$  molecules (of finite extension, that is, and attracting each other). Let the substance be split into two homogeneous phases. We introduce the following notation :

$$\begin{aligned} v_1 &= \text{volume of the first phase,} \\ v_2 &= \text{,, ,, second phase,} \\ n_1 &= \text{number of molecules in the first phase,} \\ n_2 &= \text{,, ,, ,, second phase.} \end{aligned}$$

Further, let  $f_{1\sigma}d\lambda_\sigma$  be the number of molecules per unit volume in the first phase, whose velocity points fall into  $d\lambda_\sigma$ , and similarly  $f_{2\sigma}d\lambda_\sigma$  that for the second phase.

We use for  $H$  Ornstein's expression (131), which in the present case becomes

$$H = v_1 \sum_{\sigma} f_{1\sigma} \log \frac{f_{1\sigma}}{\omega_1} d\lambda_{\sigma} + v_2 \sum_{\sigma} f_{2\sigma} \log \frac{f_{2\sigma}}{\omega_2} d\lambda_{\sigma}. \quad (146)$$

Suppose first that  $n_1, n_2, v_1, v_2$  are fixed, i.e. that the distribution of the molecules over the volume of the vessel is chosen. We are then concerned with the minimum of  $H$  with respect to the distribution of velocities only. Since through the distribution in space the potential energy is already fixed and since, as in every application of the  $H$ -theorem, the total energy must be given a prescribed value, the kinetic energy  $\epsilon'$  is also fixed. Thus (146) is to be made a minimum under the supplementary conditions

$$v_1 \sum_{\sigma} f_{1\sigma} d\lambda_{\sigma} = n_1, \quad v_2 \sum_{\sigma} f_{2\sigma} d\lambda_{\sigma} = n_2 \quad (147)$$

$$\text{and} \quad v_1 \sum_{\sigma} f_{1\sigma}^{\frac{1}{2}} m r_{\sigma}^2 d\lambda_{\sigma} + v_2 \sum_{\sigma} f_{2\sigma}^{\frac{1}{2}} m r_{\sigma}^2 d\lambda_{\sigma} = \epsilon'. \quad (148)$$

This gives

$$\delta H = v_1 \sum_{\sigma} \log \left( \frac{f_{1\sigma}}{\omega_1} - 1 \right) \delta f_{1\sigma} d\lambda_{\sigma} + v_2 \sum_{\sigma} \log \left( \frac{f_{2\sigma}}{\omega_2} - 1 \right) \delta f_{2\sigma} d\lambda_{\sigma} = 0 \quad (149)$$

with the conditions

$$\left. \begin{aligned} v_1 \sum_{\sigma} \delta f_{1\sigma} d\lambda_{\sigma} &= 0, & v_2 \sum_{\sigma} \delta f_{2\sigma} d\lambda_{\sigma} &= 0, \\ v_1 \sum_{\sigma} \frac{1}{2} m r_{\sigma}^2 \delta f_{1\sigma} d\lambda_{\sigma} &+ v_2 \sum_{\sigma} \frac{1}{2} m r_{\sigma}^2 \delta f_{2\sigma} d\lambda_{\sigma} &= 0. \end{aligned} \right\} \quad (150)$$

Whence, by the method of multipliers, similarly as in (140),

$$f_{1\sigma} = \delta_1 e^{-\frac{1}{2} m h r_{\sigma}^2}, \quad f_{2\sigma} = \delta_2 e^{-\frac{1}{2} m h r_{\sigma}^2}. \quad (151)$$

We thus find Maxwell's law for either phase. That there is but one  $h$  in both expressions, shows that the mean kinetic energy per molecule is the same in both phases.

This mean is  $\frac{3}{2h}$ , and therefore  $\epsilon' = \frac{3n}{2h}$ .

The coefficients  $\delta_1$  and  $\delta_2$  depend on the numbers of molecules  $n_1$  and  $n_2$  in the two phases. In fact, substituting in (147) the values (151) and integrating over  $d\lambda$ , we find

$$v_1 \delta_1 \left( \frac{4\pi}{3mn} \epsilon' \right)^{\frac{3}{2}} = n_1, \quad v_2 \delta_2 \left( \frac{4\pi}{3mn} \epsilon' \right)^{\frac{3}{2}} = n_2. \quad (152)$$

Next, introducing in (146) the values of  $\log f_{1\sigma}$  and  $\log f_{2\sigma}$  from (151), we find

$$\begin{aligned} H = & v_1 \log \left( \frac{\delta_1}{\omega_1} \right) \Sigma f_{1\sigma} d\lambda_\sigma - v_1 \Sigma f_{1\sigma} \frac{1}{2} m h r^2_\sigma d\lambda_\sigma \\ & + v_2 \log \left( \frac{\delta_2}{\omega_2} \right) \Sigma f_{2\sigma} d\lambda_\sigma - v_2 \Sigma f_{2\sigma} \frac{1}{2} m h r^2_\sigma d\lambda_\sigma, \\ i.e. \quad H = & n_1 \log \left( \frac{\delta_1}{\omega_1} \right) + n_2 \log \left( \frac{\delta_2}{\omega_2} \right) - h \epsilon'. \quad (153) \end{aligned}$$

In order to determine the distribution of the substance over the two phases, we have to find for what values of  $v_1$ ,  $v_2$ ,  $n_1$ ,  $n_2$  this expression becomes a minimum, while the total energy is kept constant. With the values of  $\delta_1$  and  $\delta_2$  substituted from (152), the last expression becomes

$$H = n_1 \log \frac{n_1}{\omega_1 v_1} + n_2 \log \frac{n_2}{\omega_2 v_2} - \frac{3}{2} n \log \left( \frac{4\pi}{3mn} \epsilon' \right) - \frac{3}{2} n. \quad (154)$$

Thus, what has to become a minimum is

$$n_1 \log \frac{n_1}{\omega_1 v_1} + n_2 \log \frac{n_2}{\omega_2 v_2} - \frac{3}{2} n \log \epsilon'. \quad (155)$$

Since we already know that the mean kinetic energy of a molecule is the same for both phases, we can put

$$\epsilon' = \frac{n}{n_1} \epsilon'_1 = \frac{n}{n_2} \epsilon'_2,$$

so that the last term in (155) will be replaced by

$$- \frac{3}{2} n_1 \log \left( \frac{n}{n_1} \epsilon'_1 \right) - \frac{3}{2} n_2 \log \left( \frac{n}{n_2} \epsilon'_2 \right).$$

Substituting here  $\epsilon_1' = \epsilon_1 + \frac{kn_1^2}{2\nu_1}$  and  $\epsilon_2' = \epsilon_2 + \frac{kn_2^2}{2\nu_2}$ , the expression

(155) will be seen to coincide, after the omission of constant terms, with the left-hand member of (103) with reversed sign and multiplied by  $N/R$ , the values of  $\eta_1$  and  $\eta_2$  being substituted in accordance with formula (99). We thus fall back upon the equilibrium condition which we have found before.

### 23. SUMMARY AND CONCLUSION

To sum up, we may say that we have become acquainted with three different methods of treating states of equilibrium with the aid of probability concepts. In these a "state of equilibrium" was identified with "the most probable state".

The different methods were :

1°. Boltzmann's lottery, in which account is taken of the energy condition ;

2°. Gibbs' method of microcanonic assemblages, and

3°. Boltzmann's  $H$ -theorem (generalised).

We have shown that these three methods are in essence equivalent to each other.

We have defined the entropy as a probability function, viz.  $R/N \cdot \log K$ , and this concept, which possesses all the properties of the usual thermodynamical entropy, has enabled us to treat a variety of special cases.

It cannot be denied that many of these considerations have something hypothetical about them, and the method of the  $H$ -theorem would, therefore, seem the most satisfactory one. For it can be proved rigorously, under simple assumptions about the molecules and by molecular-theory considerations (which stand above probability considerations), that the function  $H$  can do nothing but decrease. And one could inquire whether the same property holds also for the more general form

$$H = \int f \log \int_{\omega}^f dS d\lambda.$$

Presumably the answer will be in the affirmative.

## LITERATURE

The following list contains only the most important monographs. An enumeration of the papers which were published in periodicals has seemed superfluous, since exhaustive references to these are given in the works of P. and T. Ehrenfest (1911) and of A. Wassmuth (1915). The short bibliography given below has not been brought up-to-date [1923], as this would scarcely serve any purpose in connection with a course of lectures delivered in 1910-1911.

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THE THEORY OF RADIATION  
(1910-1911)



# I

## KIRCHHOFF'S LAW

THE theory of radiation is much advanced. It offers many beautiful points. It has scored some of the most brilliant successes achieved in theoretical physics. At the same time, however, it places us before the greatest difficulties.

Its foundations were laid by Kirchhoff, who first formulated the law called after him in a paper "On the relation between the emissive and the absorptive power of bodies for heat and light", published in *Ann. d. Phys. u. Chem.*, cix. p. 275, 1860. Briefly stated, this law says:—*The ratio of the emissive to the absorptive power of a body is independent of its nature.*

1. In order to define the *emissive* and the *absorptive* power of a body, we shall in the first place, following Kirchhoff, limit the radiation in question by two screens, with small apertures  $a$  and  $b$ , and consider only those rays which pass directly through these two apertures towards or from the body  $M$ .

In the next place we sort the rays according to their wavelength and put together those whose frequency  $n$  (*i.e.* the number of vibrations per  $2\pi$  seconds) falls into the interval between  $n$  and  $n + dn$ .

Finally, we choose two mutually perpendicular directions  $h$  and  $k$ , both normal (or almost so) to the direction of the rays which can pass through the apertures, and we imagine the natural rays split into two parts which are polarised along  $h$  and along  $k$ , that is to say, with  $h$  and  $k$  as the directions of vibration. Now, by the *emissive power* of the body  $M$  we mean the energy

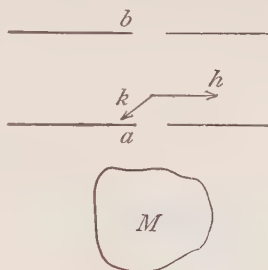


FIG. 1.

which, per unit of time, is carried away from  $M$  through the apertures by rays of frequency  $n$  to  $n + dn$  and polarised along  $h$ . This will be written

$$Edn.$$

On the other hand, the rays which pass through both apertures towards  $M$ , and which are again of frequency  $n$  to  $n + dn$  and polarised along  $h$ , can undergo various changes. They may be thrown back or taken up by  $M$ ; they may produce in  $M$  chemical actions or merely undergo a refraction and leave that body again. We shall assume, however, that *all the absorbed energy is transformed into heat*. The fraction which this forms of the whole energy incident through the apertures is called *the absorptive power* of the body and will be denoted by  $A$ .

Now, Kirchhoff's law states that *the ratio  $E/A$  is independent of the nature of the body and depends only on the frequency  $n$ , on the temperature  $T$ , and the size and relative position of the apertures*.

2. This law can be proved by means of the general thermodynamical law according to which *a system left to itself must pass into a stationary state of equilibrium*. This law enables us, for example, to correlate the pressure of saturated vapour with the curvature of the surface of a liquid, namely, by considering the equilibrium between the vapour and the curved surface of the liquid in a capillary tube. And it is again the same law which has enabled Arrhenius to find by a similar reasoning the connection between the vapour pressure and the osmotic pressure of a solution. In our case the law asserts that, if in a system a state of equilibrium of throughout equal temperature is produced, this temperature equilibrium cannot be upset by radiation.

3. Let us suppose the space surrounding the body  $M$  to be either empty or filled with a substance which is transparent to all rays (diatherman). Then we can form a good mental picture of the radiation by conceiving all the complicated vibrations as a superposition of rectilinear rays crossing each other. This is only possible under the condition that the apertures in the screen and all the bodies concerned are so large as not to give rise to diffraction. In fine, we assume that *the dimensions of the bodies and the apertures are great compared with the wave-lengths*; then the rays can be considered as rectilinear.

Much more difficult is it to form an idea about what is going on in the interior of the bodies. Rays from outside penetrate

into them and radiation comes out from their depth. But the mechanism of absorption and emission is as yet obscure. Kirchhoff's proof, however, is practically independent of what is going on inside the bodies. His proof has of late fallen somewhat into disuse: it seemed too intricate. It has been replaced by other proofs, based upon the same principle. Wien, for instance, has put the entropy at the head of the deduction. We will give here Kirchhoff's own proof somewhat simplified.

4. Kirchhoff makes use of two fictions. The first is that there are *perfectly black bodies*, which absorb, that is, and transform into heat all incident rays. In reality such bodies do not exist. Lampblack approaches this ideal closely, and platinum black still more so, but even this is not perfectly black. More recently physicists succeeded in realising the perfectly black body by a special device (cf. Art. 28).

For such a black body, of course,  $A=1$ . Let us denote the emissive power of a black body by  $e$ . Then, by Kirchhoff's law, we must have for any body whatever

$$\frac{E}{A}=e.$$

To begin with we will prove that two *different black bodies have the same emissive power*,

$$e=e'.$$

Let us imagine a black body  $M$  and two screens, provided with apertures  $a$  and  $b$ , enclosed in a box with perfectly black walls. Let the aperture  $a$  have a centre. The aperture  $b$  can be closed by either a perfectly black plate or a perfect mirror.

The existence of a *perfect mirror* is Kirchhoff's second fiction. What he means by it is a mirror which reflects all incident rays completely, unweakened, while it does not radiate itself. One might say that in this combination of properties the law to be proved is already tacitly assumed. But it must be admitted that, if a mirror which completely reflects all rays could radiate, a temperature equilibrium would be out of the question, because such a mirror would necessarily cool down.

Let it, then, be possible to close the aperture  $b$  by a perfect mirror, viz. a concave one, whose centre of curvature coincides with the centre of the aperture  $a$ .

If now the whole box, with the screens and the body  $M$ , has

throughout the same temperature, thermal equilibrium must prevail and continue to prevail, whether we shut off the aperture  $b$  with the black plate or with the hollow mirror.

If we shut it with the black plate, then everything is black, and there are no rays passing back and forth. It is true that  $M$  sends rays through  $a$  towards  $b$ , and *vice versa*, but these rays end their career by a complete absorption as soon as they reach the plate or the body  $M$ . If we now replace the black plate by the concave mirror, the body  $M$ , instead of the rays sent by the

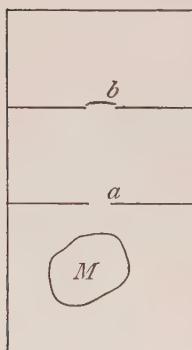


FIG. 2.

plate, receives back from  $b$  the rays which it has itself sent through  $a$  to  $b$ . The temperature equilibrium cannot be upset by this substitution. We conclude, therefore, that  $M$  radiates through  $a$  and  $b$  as much as a black plate at  $b$  would radiate through  $a$ .

If we now replace  $M$  by another black body  $M'$ , the same reasoning can be applied. What  $M'$  radiates through the apertures  $a$  and  $b$  is again equal to the energy which a black plate shutting off the aperture  $b$  would radiate through  $a$ .

Thus the total emissive power of  $M$  is equal to that of  $M'$ . If the parts corresponding to the directions of polarisation  $h$  and  $k$  are distinguished by the suffixes 1 and 2 respectively, our result can be written

$$\int (e_1 + e_2) dn = \int (e'_1 + e'_2) dn.$$

5. But this is not all. To prove that also for rays polarised along  $h$  or  $k$ , and for any frequency,  $e_1 = e'_1$  and  $e_2 = e'_2$ , a further artifice is needed. Kirchhoff looked for some means which would enable him to discriminate in his reasoning between rays of different wave-length. And he found this in a thin *plane-parallel plate* which, owing to *interference*, reflects rays of different wave-lengths with different intensities. Let us imagine such a plate, and let this be perfectly diatherman, and thus neither absorbing nor radiating. Its thickness, which is of the order of a wave-length, can, in accordance with Art. 3, be neglected in comparison with the dimensions of the screens, etc., in our black box. Let



us now place this interference plate at  $P$  under the angle of polarisation. The latter will be assumed to be the same for rays of all wave-lengths. We put the plane of incidence perpendicularly to the direction  $h$ . In this manner we obtain that *only rays which are polarised along  $h$  are reflected*. Further, we place the plate so that  $a'$  and  $b'$ , the images of  $a$  and  $b$ , fall upon the walls of the box.

We shall keep the aperture  $b$  always closed by a black plate, while at  $b'$  we shall imagine now a black plate and now a perfect concave mirror having its centre at the centre of  $a'$ . An auxiliary screen placed near  $a$  prevents the rays from passing directly from  $b'$  through  $a$ .

Now, whether we leave at  $b'$  the black plate or replace it by the mirror, the temperature equilibrium will not be upset. And the equilibrium will still persist, if instead of  $M$  another black body  $M'$  is placed below  $a$ .

By removing the black plate from  $b'$  we deprive  $M$  of the radiation which this body was receiving from it through the plate  $P$  across the aperture  $a$ . This radiation is independent of the nature of  $M$ . If we now introduce the mirror, the body receives, in the first place, the radiation which issues from  $a'$ , falls upon the mirror and after a reflection at  $P$  reaches  $M$  through  $a$ . This again is independent of  $M$ . In the second place,  $M$  receives its own radiation, which through  $P$  arrives at  $b'$  and then through  $P$  and  $a$  returns to  $M$ . Ultimately, therefore, also this must be independent of the nature of  $M$ .

Thus, if the coefficient of reflection of the plate for vibrations normal to the plane of incidence be denoted by  $r$ , we shall have

$$\int e_1 r^2 dn = \int e'_1 r^2 dn.$$

Now, by taking, for instance, plates of different thickness the case may be so varied that  $r$  will be now one and now another function of  $n$ . The last equation will always hold good. Whence Kirchhoff concludes that, *for all frequencies*,

$$e_1 = e'_1.$$

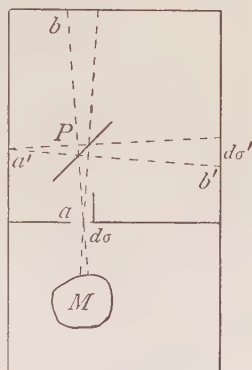


FIG. 3.

If we take for  $M'$  the original black body  $M$ , but turned about the central axis of  $a$  and  $b$  through a right angle, then we have to put  $e_2$  instead of  $e'_1$ .

We thus see that also  $e_1 = e_2$ , and similarly  $e'_1 = e'_2$ .

This means that *the radiation of a black body is unpolarised*.

A similar reasoning would also show us at once that the *emissive power is independent of the place at which the black body is located and independent of its orientation*.

6. We will now apply what precedes to *the reciprocal radiation of black plates*. Let us imagine the black body  $M$  in the form of a plate of size (area)  $d\sigma$  which just fits into the aperture  $a$ . How much energy will this plate radiate per second towards another black plate  $d\sigma'$  which just fits into the aperture  $b$ ?

By what precedes this will be  $edn$  for radiation of the frequency interval  $dn$ .

Take first the case in which the plates are normal to their join, at a distance  $r$  from each other.

The energy radiated by any small element of  $d\sigma$  towards  $d\sigma'$  will be proportional to the solid angle  $d\omega$  of the cone subtended by  $d\sigma'$ . If the dimensions of  $d\sigma$  are small compared with  $r$ , the difference of this solid angle for different elements of  $d\sigma$  can be neglected as a small quantity of higher order. Hence it is not difficult to see that the energy radiated by  $d\sigma$  to  $d\sigma'$  is proportional to  $d\sigma$  and to  $d\omega$ . If we write

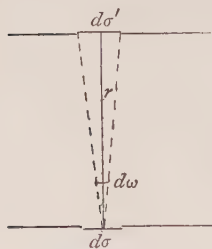


FIG. 4.

$$edn = qd\sigma d\omega dn,$$

then  $q$  can evidently no longer depend on the nature and the dimensions of the black plate; it will depend only on the temperature and the frequency  $n$ .

If the solid angle  $d\omega$  is expressed in terms of  $d\sigma'$  and  $r$ , we have

$$edn = \frac{qd\sigma d\sigma' dn}{r^2}.$$

In this formula  $d\sigma$  and  $d\sigma'$  occur in exactly the same way; which exhibits a certain *reciprocity*. In fact, a reasoning in which, as before,  $d\sigma'$  is supposed to be replaced by a perfect concave mirror would show at once that  $edn$  is also the energy which  $d\sigma'$  radiates to  $d\sigma$ .

One might consider it as self-evident that two black plates in temperature equilibrium send to each other equal amounts of energy. But Kirchhoff was particularly anxious to deal in his proof always with a completely closed system.

We have still to extend our result to the case in which the two plates, instead of being perpendicular to their join, have their normals inclined to it at any angles  $\theta$  and  $\theta'$ . We shall prove that in this general



FIG. 5.

case the mutual radiation of the black plates is expressed by

$$q \frac{\cos \theta \cos \theta' d\sigma d\sigma'}{r^2} dn.$$

In fact, since the orientation of the receiving plate  $d\sigma'$  is determined by the angle  $\theta'$ , the aperture  $d\omega$  of the cone of rays issuing from  $d\sigma$  is

$$d\omega = \frac{\cos \theta' d\sigma'}{r^2},$$

and if the radiating plate  $d\sigma$  were placed obliquely behind the aperture  $a$ , it would send to  $d\sigma'$  through this aperture as much energy as another plate parallel to the aperture, but of size  $d\sigma \cos \theta$ . This follows from Kirchhoff's law which we have just

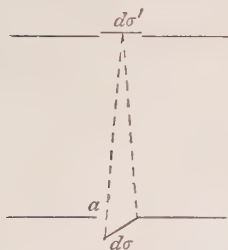


FIG. 6.

proved for black bodies, and according to which the emissive power of a black body through the two apertures is independent of its position. In fact, we see at once (Fig. 6) that when a black plate is placed behind the aperture  $a$  obliquely, the part of its surface which contributes to the radiation through the two apertures is greater than if the plate were placed normally to the direction of the rays, whereas

the amount of radiation should be the same in both cases. This is taken care of by the factor  $\cos \theta$ .

Notice that from Kirchhoff's law for a black body follows here the known law of Lambert, which says that the light emitted by a surface element of a diffuse radiator within a cone of infinitesimal aperture is proportional to the cosine of the angle between the axis of the cone and the normal of that element. In accordance

with this law a glowing ball appears to the eye uniformly bright, from the centre to the rim.

7. In his farther reasoning Kirchhoff makes use of a lemma, a *reciprocity theorem*, which is an extension of the preceding one. It may occur that the rays emitted from a black plate reach a second black plate only after having been refracted or reflected by a number of other bodies. In this case energy will also be abstracted from the rays by absorption or scattering. Now, Kirchhoff asserts that, no matter how the rays were refracted or reflected, the energies which the two black plates mutually receive from each other per unit of time will be equal.

We shall return to this reciprocity theorem later on, in Art. 11.

8. Let us now derive *Kirchhoff's law for any, not black bodies*.

We turn again to the previous arrangement. We imagine the body  $M$  in the box with black walls (Fig. 3) below the aperture  $a$  of the screen, above which is placed a thin interference plate  $P$ . This plate reflects only the rays polarised along the direction  $h$ , and throws upon the black walls of the box images,  $a'$  and  $b'$ , of the apertures  $a$  and  $b$ .

By the fundamental thermodynamical law the temperature equilibrium can undergo no change, if a portion of the black wall at  $b'$  is replaced by a perfect concave mirror, whose centre may again coincide with the midpoint of  $a'$ .

Now, by removing a small portion of the wall at  $b'$  we subtract from the radiation absorbed, per unit time, by the body  $M$  the amount

$$eArdn,$$

where  $A$  is the absorptive power of  $M$  and  $r$  the coefficient of reflection of  $P$  for rays of frequency  $n$ . In fact, the amount radiated by that portion at  $b'$  towards  $a'$  is  $edn$ .

On the other hand, introducing the concave mirror, we add to the radiation absorbed by the body :

1°. A quantity, coming from  $a'$ , which follows the path  $a'Pb'Pa$  and is finally absorbed by  $M$  ; this amounts to

$$e(1-r)Adn ;$$

2°. A quantity which starts from  $M$  itself and returns to it along the path  $MPb'Pa$  ;  $Edn$  being the emissive power of  $M$ , as defined in Art. 1, this contribution amounts to

$$Er^2Adn ;$$

3°. A quantity which is due to the black walls around  $M$ , and which finds its way through  $M$  and follows along the path  $aPb'Pa$  to be again absorbed in  $M$ . Its amount cannot be found directly. But here comes in the reciprocity theorem. The energy in question, emitted by different elements  $d\sigma''$  of the black walls through the aperture  $a$  upwards, would in absence of  $P$  fall entirely upon the black plate which shuts off the aperture  $b$ . In virtue of that theorem this is equal to the energy due to the plate at  $b$ , which would reach the elements  $d\sigma''$  of the black walls. The energy which flows through  $a$  upwards and with which we are concerned is thus

$$e(1-A)dn.$$

Of this energy, after it covered the path  $aPb'Pa$ , the body  $M$  absorbs

$$e(1-A)r^2Adn,$$

which is the required amount.

If we still assume that of the radiation which falls upon  $M$  through the aperture  $a$  nothing returns upwards through  $a$  by either reflection or refraction (an assumption which will readily be granted), then we have all that is needed to calculate how much more (or less) energy the body  $M$  absorbs after the introduction of the concave mirror at  $b'$  than before. The condition that the temperature equilibrium shall persist is

$$\int eArdn = \int e(1-r)rAdn + \int Er^2Adn + \int e(1-A)r^2Adn$$

or 
$$\int (E - eA)r^2Adn = 0.$$

The thickness of the interference plate can be varied at will, so that  $r$  will be now one and now another function of the wavelength. The equation must always hold good. Whence Kirchhoff concludes that, for each frequency,

$$E - eA = 0$$

or 
$$\frac{E}{A} = e,$$

which was to be proved.

The beauty of Kirchhoff's law and of its proof as given by him lies mainly therein that  $E$  and  $A$  are determined with much



precision by fixing so sharply the limitation of the contemplated radiation, its wave-length and state of polarisation also being unambiguously specified.

9. A consequence of this law is that, if certain bodies have different emissivities, we know also at once what their absorptive power will be like, and *vice versa*.

9, 1. If it be assumed that all bodies absorb of all rays something, no matter how little, then they should have also for all rays [wave-lengths] a certain emissive power, so far at least as the perfectly black body has at the same temperature some emissive power for the rays in question. And if one body begins to glow, *i.e.* to send out red rays, at a given temperature, then also all bodies should begin to glow at the same temperature (Draper's law), unless they do not at all absorb the red rays. Thus, for example, a strongly heated *salt droplet* in a platinum loop gives out no light, because it is translucent and does not itself absorb, while the platinum wire does. On the other hand, an *ink spot* on a glowing platinum plate radiates more light than the platinum.

9, 2. Again, we may be sure that the light emitted by a glowing *tourmaline plate* will be partially polarised, with a predominance of vibrations of that direction which are also more strongly absorbed by the tourmaline plate.

9, 3. Suppose we investigate the emissivity of a body for rays of different wave-lengths and that, while for the black body  $e$  varies in the given region but moderately,  $E$  for our body shows strong variations, that *e.g.* it becomes suddenly very large to drop then again to a low value. Then also its absorptive power will vary in the same way. Yet we must be careful and not think, for instance, that from Kirchhoff's law for sodium vapour follows necessarily the reversal of spectrum lines, that is to say, the fact that in the absorption spectrum we see as black lines what in the emission spectrum of sodium appeared as bright lines,—the first principle upon which the *spectrum analysis of stars* is based. Such a conclusion would not be legitimate for all spectrum lines, because the circumstances of light emission by sodium vapour, in flames and in electrical discharges, do not warrant the thermodynamical equilibrium; in these processes there may, *e.g.*, come into play chemical actions which were at the outset excluded from our considerations.



10. As regards the rôle played in emission by *the surface* of a body, we may notice that every circumstance which favours absorption will enhance also the emission, and *vice versa*. Absorption takes place always *inside* the body, though it may be located just below its surface. Thus also does a body always radiate from its innermost. The deeper layers, however, contribute less to absorption for the simple reason that the amount of radiation arriving there from without is so much less. They contribute also less to the emission because only a small part of what they radiate can reach the surface and pass outward.

In metals the absorption takes place in an extremely thin layer. Accordingly, the same thin layer only takes part in the emission.

The metals absorb so little because they reflect so much. Thus they ought also to radiate but little. We have here to keep in mind that the rays which fall upon the surface from within are reflected to the same extent as those incident from without. In fact, the coefficient of reflection is the same, whether the rays are reflected at the inner or the outer side of the surface. For a piece of glass, say, this coefficient is, according to Fresnel,

$$\frac{\sin^2(i-r)}{\sin^2(i+r)} \text{ and } \frac{\tan^2(i-r)}{\tan^2(i+r)}$$

for light vibrations perpendicular and parallel to the plane of incidence respectively, if  $i$  be the angle of incidence and  $r$  that of refraction. Now, these values remain unaltered by a permutation of  $i$  and  $r$ .

The coefficients of reflection being different according to the polarisation of the rays, the light emitted in oblique directions must be partially polarised.

11. *The weak point* of Kirchhoff's proof is *the reciprocity theorem* (Art. 7). In using it Kirchhoff bases himself upon Helmholtz, who enunciated the theorem in his *Physiological Optics*. Kirchhoff gives no proof.

If the bodies which are placed in the path of the rays which the two black plates send to each other are perfectly transparent, then the theorem can indeed be proved. It then has a geometrical character. Clausius has applied it in order to show that it is impossible by means of properly chosen lens systems so to concentrate pencils of rays, as to raise the temperature of a body

at the expense of another body which initially had the same temperature, and thus to overthrow the second law of thermodynamics (cf. Art. 17, *infra*).

If the inserted bodies are not diatherman, the reciprocity theorem could still be proved, but not without making certain assumptions about the nature of the bodies.\*

Thus in the proof of Kirchhoff's law the nature of the bodies would come into play, whereas the law has just to hold good independently of the nature of the bodies. At any rate, in the deduction given by Kirchhoff, viz. in the application of the reciprocity theorem, something is assumed which is difficult to prove, and precisely for that body for which the law is to be deduced.

There is, however, another theorem, still more important than Kirchhoff's law, which Kirchhoff, to be sure, deduces from the latter, but which can also be arrived at directly without making use of the reciprocity theorem and which can entirely replace Kirchhoff's law.

12. This important theorem says that *a given radiation can be in equilibrium with all bodies of one and the same temperature.*

The state of radiation in a space containing nothing but the aether can be determined as follows. Consider (Fig. 7) a surface element  $d\sigma$ , an infinitely narrow cone  $d\omega$  whose axis  $ab$  is normal to  $d\sigma$ , and a given direction  $h$  perpendicular to  $ab$ . Owing to the radiation within the cone  $d\omega$  there will pass through  $d\sigma$ , per unit time, a certain amount of energy of frequency contained between  $n$  and  $n+dn$  and with the direction of vibrations  $h$ . If this energy be given for each element  $d\sigma$ , for each cone  $d\omega$ , each direction of vibration  $h$ , and each interval  $dn$ , the state of radiation can be said to be completely known. The radiation thus defined will be called briefly the  $(d\sigma, d\omega, h, dn)$ -radiation.

This radiation can readily be determined, if the cone  $d\omega$ , produced beyond  $d\sigma$ , hits a perfectly black body, e.g. a black wall. Let it cut out an element  $d\sigma'$  of the wall, let the normal to the latter make an acute angle  $\theta'$  with the axis of the cone, and let  $r$  be the distance of  $d\sigma'$  and  $a$ , the centre of  $d\sigma$ . Then

\* H. A. Lorentz, "Over de warmtestraling in een stelsel lichamen van overal gelijke temperatuur", *Zitt. versl. K. Ak. v. Wetensch.*, Amsterdam, 1905, p. 345 and p. 408.

the  $(d\sigma, d\omega, h, dn)$ -radiation can be replaced by the  $(h, dn)$ -radiation which passes from  $d\sigma'$  through  $d\sigma$ . This is, by Art. 6,

$$\frac{qd\sigma d\sigma' \cos \theta' dn}{r^2},$$

or also

$$qd\sigma d\omega dn.$$

The coefficient  $q$  depends only on the frequency  $n$  and the temperature  $T$ . If a portion of the aether is completely enclosed by black walls, this expression holds for all  $d\sigma$ ,  $d\omega$ ,  $h$ , and  $dn$ . The radiation is then *unpolarised* and of *isotropic* and *homogeneous* distribution. This is called *black radiation*, though the name is not quite appropriate when the temperature is so high that the black walls emit also visible light.

Let us still note that the state of black radiation is not disturbed by

the introduction of a thin, perfectly transparent plate. This can be proved without trouble by noticing that, when the cone  $d\omega$  strikes the plate, the  $(d\sigma, d\omega, h, dn)$ -radiation comes not only from the element  $d\sigma'$  already considered but also, after reflection, from another element  $d\sigma''$  of the black wall. Thus, if  $r$  and  $1 - r$  be the reflecting and the transmitting power of the plate, the element  $d\sigma'$  will contribute to the  $(d\sigma, d\omega, h, dn)$ -radiation the amount  $(1 - r)qd\sigma d\omega dn$ , and the element  $d\sigma''$  the amount  $rqd\sigma d\omega dn$ , so that ultimately the transparent plate will produce no disturbance.

13. To prove the theorem enunciated above, we place an arbitrary body  $M$  of temperature  $T$  within a black enclosure of the same temperature and distinguish in the sequel between rays falling upon and rays coming from the body. We exclude the case in which the rays from one part of the body fall directly upon another part. We thus assume the surface of the body to be everywhere convex.

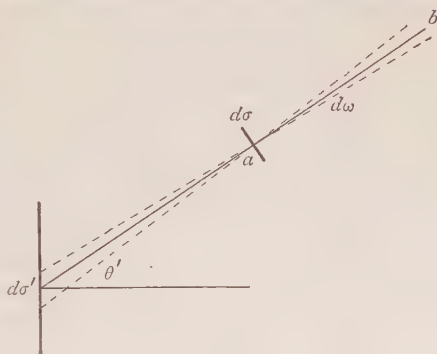


FIG. 7.

The radiation falling upon the body is exclusively black radiation. It is independent of the shape and the position of the surrounding walls.

The radiation "going out" from the body consists of its own rays, emitted by its internal volume elements, and of rays which indirectly come from the black walls. The body being entirely surrounded by black walls, the latter as well as the former rays must be completely determined and will be independent of the position of the walls.

What we want to prove is that *the radiation of the body can be expressed by  $q d\sigma d\omega dn$* .

14. We proceed as before (Fig. 8). We cut out of a black

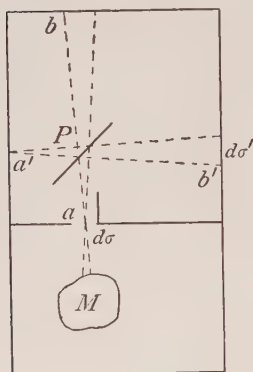


FIG. 8.

screen an aperture  $d\sigma$  which we choose so that the cone  $d\omega$  produced hits the body, and we place in front of  $d\sigma$  a thin plate ( $P$ ) under the angle of polarisation and parallel to the chosen direction  $h$  of vibrations; next, we enclose everything by black walls in such a way that the axis of the cone  $d\omega$ , after a reflection at the plate, strikes the wall perpendicularly. Let  $d\sigma'$  be the element of the black wall thus hit by the cone  $d\omega$  whose vertex lies at the centre of  $d\sigma$ . In accordance with what was said in Art. 12, neither the rays falling upon the body nor the

$(d\sigma, d\omega, h, dn)$ -radiation emitted by it will undergo any change whatever due to the introduction of the plate. If we write for the amount of the latter radiation

$$q' d\sigma d\omega dn,$$

we have to prove that  $q' = q$ .

Now, replace  $d\sigma'$  by the repeatedly mentioned concave mirror. This will produce a change in the  $(d\sigma, d\omega, h, dn)$ -radiation which falls upon the body, and thus also the rays (due originally to this radiation) which the body re-emits upwards, and which we count to its "outgoing" rays, might be altered. But if, as did Kirchhoff in proving his law, we make the assumption that of the incident  $(d\sigma, d\omega)$ -radiation no perceptible part is to be found in

the outgoing  $(d\sigma, d\omega)$ -radiation, then the outgoing  $(d\sigma, d\omega, h, dn)$ -radiation will remain the same, *i.e.* still

$$q'd\sigma d\omega dn.$$

Thus it remains only to find the change in the radiation falling upon the body. Now, replacing  $d\sigma'$  by the mirror we take away the amount

$$qrd\sigma d\omega dn$$

which fell, per unit time, from  $d\sigma'$ , via  $P$  and  $d\sigma$ , upon the body. On the other hand we add what comes from  $a'$  via  $P$ ,  $d\sigma'$ ,  $P$ ,  $d\sigma$  and from  $M$  itself via  $d\sigma$ ,  $P$  and so on along the same path, *i.e.*

$$q(1-r)rd\sigma d\omega dn \text{ and } q'r^2d\sigma d\omega dn.$$

Thus the radiation which falls upon the body decreases by

$$(q - q')r^2d\sigma d\omega dn,$$

and the part of it which the body receives diminishes by

$$(q - q')Ar^2d\sigma d\omega dn.$$

In all, therefore, the body  $M$  absorbs less than originally by the amount

$$d\sigma d\omega \int (q - q')Ar^2dn.$$

Now, if this is to vanish, for  $r$  any function of  $n$ , as required for the persistence of the temperature equilibrium, we must have

$$q' = q,$$

which was to be proved.

15. Thus, if a body is placed within a black enclosure, so that it is exposed on all sides to *black radiation*, it is *in equilibrium with it, no matter what its own nature may be*. Whence can be deduced the parallelism between the emissive and the absorptive power of the body, as expressed by Kirchhoff's law. In fact, if the body emits less, then, since the energy of the rays emerging from the body does not depend on its nature, that part of the outgoing energy which comes indirectly from the walls must be greater, so that the body must also absorb less.

16. We shall now prove that *the black radiation* within a black enclosure is *not altered* when a part of the enclosure is replaced by a *perfect mirror*.

In the case of reflection at a *plane mirror* we can see at once that the black radiation remains black radiation. In fact, what



after reflection passes through an element  $d\sigma$  within a cone  $d\omega$  would in absence of the mirror pass through an element  $d\sigma'$ , and within a cone  $d\omega'$  which are mirror images of  $d\sigma$  and  $d\omega$ . The amount of the  $(d\sigma, d\omega, h, dn)$ -radiation is thus equal to that of the  $(d\sigma', d\omega', h', dn)$ -radiation, *i.e.* to  $qd\sigma'd\omega'dn$ , which, in view of the geometrical equality of the elements and their images, is equal to  $qd\sigma d\omega dn$ . But this means that the  $(d\sigma, d\omega, h, dn)$ -radiation is black radiation.

17. When we turn to the case of an *arbitrarily curved, concave or convex mirror*, we are brought into contact with a beautiful theorem, which was first derived by Clausius to meet the objection that heat radiation could be concentrated by means of lenses and mirrors from a cold towards a hot body, thus giving a continuous transfer of heat from the former to the latter, against the second law of thermodynamics formulated by him. This theorem is connected with an optical theorem due to Lagrange, *i.e.* with the relation

$$hn\epsilon = h'n'\epsilon'$$

between the linear dimensions  $h$  and  $h'$  of two images [object and image] in a centred lens system, the refractive indices  $n$  and  $n'$  of the media in which the images lie, and the angles  $\epsilon$  and  $\epsilon'$  between two given light rays diverging or converging at a point of either image—a relation which in a different form was already known to Huygens.

18. The proof is based upon the theorem that, when a ray is reflected, *the path followed is a minimum*. Let  $ACB$  be the

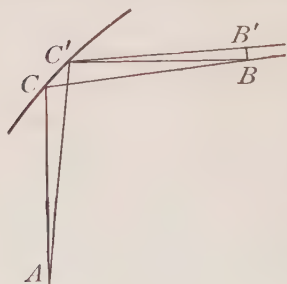


FIG. 9.

path of a light ray, and  $AC'B$  another, infinitesimally different, path. Then, no matter on which side  $C'$  lies,  $ACB$  will always be the shortest path. Thus, up to a difference of the second order,  $ACB$  and  $AC'B$  are equal to each other. Let  $l$  be the length of either path. Consider a number of rays diverging from a point  $A$  and cut off on each of them (*i.e.* from  $A$  to the mirror and then along the

reflected ray) equal segments. Then their end-points will lie upon a certain surface, the wave surface, to which all the rays



are perpendicular. In fact, if  $AC'B'$  be a neighbouring ray, we have, by construction,  $AC + CB = AC' + C'B'$ . But, by the minimum property,  $AC + C'B = AC' + C'B$ , so that  $C'B' = C'B$ , and since the angle  $BC'B'$  is infinitesimal, it follows that the angle at  $B'$  is a right angle.

This shows us how the length of path  $l$  changes when  $B$  is displaced by  $dh$  in any direction  $h$  to  $B''$ , so that the new path is from  $A$  to  $B''$ . The change vanishes if  $h$  is perpendicular to the direction of the ray  $CB$ , and it attains a maximum if  $h$  coincides with the direction of the ray. In general we have

$$\frac{\partial l}{\partial h} = \cos(l, h),$$

where  $(l, h)$  is the angle between the direction of the ray  $(l)$  and  $h$ .

19. Now, in order to derive *Clausius's theorem*, consider two planes  $U$  and  $V$  which pass through  $A$  and  $B$ , and introduce two systems of co-ordinates,  $x_1, y_1$  in  $U$  and  $x_2, y_2$  in  $V$ .

A ray passes from each point  $(x_1, y_1)$  of  $U$  to a point  $(x_2, y_2)$  of  $V$ .

The length  $l$  of this ray

is a function of  $x_1, y_1, x_2, y_2$ . By the last formula,

$$\frac{\partial l}{\partial x_2} = \cos(l, x_2), \quad \frac{\partial l}{\partial y_2} = \cos(l, y_2).$$

If  $BQ$  be a segment of unit length cut off on the ray arriving at  $B(x_2, y_2)$ , and  $K$  the projection of  $Q$  upon  $V$ , then the co-ordinates of  $K$  with respect to  $B$  are

$$x_{2k} - x_2 = \xi_2 = \cos(l, x_2), \quad y_{2k} - y_2 = \eta_2 = \cos(l, y_2)$$

or

$$\xi_2 = \frac{\partial l}{\partial x_2}, \quad \eta_2 = \frac{\partial l}{\partial y_2}.$$

These are functions of  $x_2, y_2$ , as well as of  $x_1, y_1$ , the co-ordinates of the point  $A$  in the plane  $U$  which is the origin of the ray. If  $A$  moves over a surface element  $d\sigma_1$ , the ray arriving

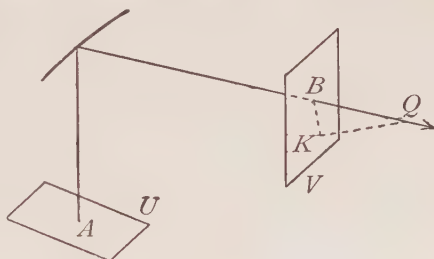


FIG. 10.

from  $A$  at  $B$  describes a cone of aperture  $d\omega_2$ . The point  $Q$  describes, therefore, an area  $d\omega_2$ , and if  $\theta_2$  be the acute angle between the axis of the cone and the normal of  $V$ , the surface element described by the point  $K$  ( $\xi_2, \eta_2$ ), the projection of  $Q$  upon  $V$ , is  $\cos \theta_2 d\omega_2$ . Thus  $d\sigma_1$  and  $\cos \theta_2 d\omega_2$  are the elements simultaneously described by the points  $(x_1, y_1)$  and  $(\xi_2, \eta_2)$ . Hence, their ratio is given by the functional determinant, *i.e.*

$$\cos \theta_2 d\omega = d\sigma_1 \begin{vmatrix} \frac{\partial \xi_2}{\partial x_1} \frac{\partial \xi_2}{\partial y_1} \\ \frac{\partial \eta_2}{\partial x_1} \frac{\partial \eta_2}{\partial y_1} \end{vmatrix}$$

or, by the last formulae,

$$\cos \theta_2 d\omega_2 = d\sigma_1 \begin{vmatrix} \frac{\partial^2 l}{\partial x_1 \partial x_2} & \frac{\partial^2 l}{\partial y_1 \partial x_2} \\ \frac{\partial^2 l}{\partial x_1 \partial y_2} & \frac{\partial^2 l}{\partial y_1 \partial y_2} \end{vmatrix}.$$

A similar formula is obtained by considering the rays from  $A$  within a cone  $d\omega_1$  making an angle  $\theta_1$  with the normal of the plane  $U$ , and the element  $d\sigma_2$  which these rays cut out of the plane  $V$ . The determinant is in both cases the same. Thus we have

$$\frac{\cos \theta_2 d\omega_2}{d\sigma_1} = \frac{\cos \theta_1 d\omega_1}{d\sigma_2}$$

$$\text{or} \quad \cos \theta_2 d\sigma_2 d\omega_2 = \cos \theta_1 d\sigma_1 d\omega_1.$$

This contains *Clausius's theorem*.

20. In fact, from this equation it follows that *black radiation remains black after reflection*. For, up to an infinitesimal difference of higher order, the rays which after reflection pass through  $d\sigma_2$  within the cone aperture  $d\omega_2$  are the same as those which before and after the reflection pass through  $d\sigma_1$  and  $d\sigma_2$ , and these are again the same as those passing through  $d\sigma_1$  within the cone  $d\omega_1$ . Since the latter carry with them the energy

$$q \cos \theta_1 d\sigma_1 d\omega_1 dn,$$

the rays after reflection must carry as much energy through  $d\sigma_2$ . But, by the last equation, this is equal to  $q \cos \theta_2 d\sigma_2 d\omega_2 dn$ , which means that the radiation through  $d\sigma_2$  is black radiation. For the sake of completeness the directions of polarisation for

the incident rays in and perpendicular to the plane of incidence could still be assigned. To these correspond in the reflected rays again two mutually perpendicular directions of polarisation.

From what has just been proved it follows that the state of radiation is not altered if a body of temperature  $T$ , instead of being surrounded by black walls of the same temperature, is placed within a perfectly reflecting enclosure.

21. It could still be proved without trouble that, if in the enclosed space are placed various *transparent bodies* which *refract* only the rays without absorbing them, *the black radiation remains black*. The proof is exactly as before. Of the different paths leading from  $A$  to  $B$  the ray will now pass along that which requires the shortest time (Fermat's theorem). This time, which is a function of the co-ordinates of  $A$  and  $B$ , takes the place of the length of path in the previous reasoning.

Herewith the derivation of Clausius's theorem would be completed.

At first sight one might think that the last theorem is already contained as a consequence in that proved before, viz. that each body can be in equilibrium with the black radiation. But in the proof of this theorem it was assumed that the absorptive power  $A$  of the body is different from zero. Now, for a diatherman lens, say,  $A$  would be zero, so that nothing could be proved about its equilibrium. A diatherman substance could also be in equilibrium with non-black radiation.

22. Lastly, let us find the expression for *the black radiation within a transparent body*, as, *e.g.*, in a piece of diatherman glass. As in the aether, there will be also in glass a tangle of rays. The state of radiation will again be determined by assigning the energy of a  $(d\sigma, d\omega, h, dn)$ -radiation, as in the case of the aether. If this energy be

$$q' \cos \theta d\sigma d\omega dn,$$

we have to find what relation must hold between  $q'$  and  $q$  in order that the state of radiation within the glass shall be in equilibrium with that prevailing outside. If  $\mu$  be the refractive index, we shall find

$$q' = \mu^2 q.$$

In fact, take for  $d\sigma$  an element of the (plane) boundary and consider the rays which impinge upon it within the cone aperture

$d\omega$ . These will fill out in the glass an elementary cone  $d\omega'$ . A geometrical consideration will show that

$$d\omega : d\omega' = \frac{\mu^2}{\cos \theta} : \frac{1}{\cos \theta'}.$$

Let the infinitesimal cones be determined by the azimuth intervals  $d\phi$  and  $d\phi'$ , and by the intervals  $d\theta$  and  $d\theta'$  for the angles with the normal. Then  $d\phi$  and  $d\phi'$  will be equal and, by the law of refraction,

$$\sin \theta = \mu \sin \theta'.$$

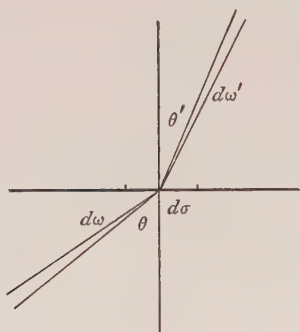


FIG. 11.

The apertures of the cones are to each other as  $\sin \theta d\theta d\phi$  to  $\sin \theta' d\theta' d\phi'$ , whence the above relation follows at once.

Now, the energy streaming towards  $d\sigma$  in the aether, with vibrations perpendicular to the plane of incidence, is, per unit time,  $q \cos \theta d\sigma d\omega dn$ . Of this penetrates into the glass the amount  $(1-r)q \cos \theta d\sigma d\omega dn$  or

$$(1-r)q\mu^2 \cos \theta' d\sigma d\omega' dn.$$

The rays within the glass which are directed towards  $d\sigma$  and are thrown back within  $d\omega'$  carry the energy  $q' \cos \theta' d\sigma d\omega' dn$ , of which is reflected the amount

$$r'q' \cos \theta' d\sigma d\omega' dn.$$

This, together with the amount coming from outside, must be equal to what corresponds to the black radiation within the glass. Thus

$$(1-r)q\mu^2 \cos \theta' d\sigma d\omega' dn + r'q' \cos \theta' d\sigma d\omega' dn = q' \cos \theta' d\sigma d\omega' dn.$$

By Fresnel's reflection formulae,  $r' = r$  for each direction of vibration. Thus,

$$(1-r)q\mu^2 - (1-r)q',$$

and therefore,

$$q' = \mu^2 q,$$

which was to be proved.

## II

### BOLTZMANN'S LAW

23. We have now sufficiently explained how the state of black radiation is characterised by the expression

$$q d\sigma d\omega dn,$$

which indicates the amount of energy carried per unit time across the surface element  $d\sigma$  within a cone of aperture  $d\omega$ , perpendicular to this element, by rays which are polarised in a certain direction and whose frequency falls within the interval  $(n, n + dn)$ .

In this expression  $q$  is a function of the frequency  $n$  and the temperature  $T$ , whose form we wish to find.

24. The energy which in the short time  $dt$  flows across  $d\sigma$  within  $d\omega$  occupies an infinitesimal cylinder of base  $d\sigma$  and height  $c dt$ , and thus of volume  $c d\sigma dt$ , if  $c$  be the velocity of propagation of the rays. Consequently the amount of this energy per unit volume is

$$\frac{q}{c} d\omega dn.$$

If we count also the energy of the rays polarised in the other (perpendicular) direction, this amount will be doubled. To find the complete energy per unit volume of the black radiation, we have to integrate over  $d\omega$ , remembering that the radiation is isotropic. *Thus the density of energy of the black radiation for the frequency interval  $(n, n + dn)$  is found to be*

$$u dn = \frac{8\pi q}{c} dn,$$

and ultimately, *the total density of energy,*

$$U = \int_0^\infty u dn = \frac{8\pi}{c} \int_0^\infty q dn.$$

The state of radiation is of course characterised by  $u$  as well as by  $q$ . This  $u$  is again a function of  $n$  and  $T$ , which we shall endeavour to derive.

25. The first step made in this direction has taught us that *the density  $U$  of the total energy of radiation is proportional to the fourth power of the temperature*. This is *Boltzmann's law*,\* a brilliant achievement of modern physics. It can be arrived at by applying the second law of thermodynamics.

Let us imagine a space, closed by walls impermeable to heat, in which a body  $M$  produces the state of black radiation. What we have here resembles very much a gas filling a closed space. The radiation as well as the gas exerts a pressure upon the walls. A cylinder containing gas can be taken through a Carnot cycle of changes. In a similar way this can also be done with our space filled with radiation, if it is shut off by a piston. When the piston is pulled back, the radiation pressure does work upon it. Also, the newly evacuated volume is being filled with radiation. The energy is supplied by the body  $M$  which can be in contact with a heat reservoir. The opposite takes place when the piston is pushed in. It is easy to imagine how adiabatic and isothermic compressions and expansions could be arranged.

Instead of a Carnot cycle, however, we will just now make use of a more modern thermodynamical formula.

26, 1. In the first place we must enter more nearly upon the meaning of *the radiation pressure*. Here we borrow what we need from the electromagnetic theory. Suppose that a pencil impinges obliquely upon a perfectly reflecting surface, under an angle  $a$  to the normal (Fig. 12). Consider the electromagnetic radiation pressure acting in a cross-section of the incident and of the reflected pencil, which must be balanced by the external pressure exerted on the portion  $\Sigma$  of the surface hit by the pencil. If  $a$  be the amplitude of the rays,

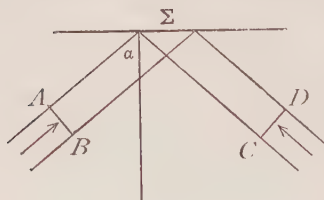


FIG. 12.

\* L. Boltzmann, "Ableitung des Stefan'schen Gesetzes betreffend die Abhängigkeit der Wärmestrahlung von der Temperatur aus der elektromagnetischen Lichttheorie", *Ann. Phys. Chem.* xxii. p. 291, 1885.



the normal pressure upon  $AB$  and  $CD$  will be  $\frac{1}{2}a^2$  per unit area. Thus the pressure upon  $\Sigma$  will amount to

$$2\Sigma \cos \alpha \cdot \frac{1}{2}a^2 \cos \alpha,$$

and the pressure per unit area of the reflecting surface would be  $2 \cos^2 \alpha$  times the density of energy ( $\frac{1}{2}a^2$ ) in the incident pencil. Consequently the rays of frequency  $(n, n + dn)$  incident within the cone of aperture  $d\omega$  contribute per unit area of the reflecting wall a pressure which, for both directions of polarisation, amounts to

$$\frac{4q}{c} dn \cos^2 \alpha d\omega.$$

To find the total radiation pressure we have to integrate over all incident pencils of rays. Take for the cone  $d\omega$  all the rays whose incidence angles are contained between  $\alpha$  and  $\alpha + d\alpha$ , so that

$$d\omega = 2\pi \sin \alpha d\alpha,$$

and integrate over  $\alpha$  from  $0$  to  $90^\circ$ . This will give for the pressure due to the rays of frequency  $(n, n + dn)$

$$\frac{8\pi q}{3c} dn = \frac{1}{3} u dn,$$

and the total radiation pressure will be one-third of the total density of energy,

$$p = \frac{1}{3} U.$$

26, 2. This result can also be readily obtained by another method. In the case of a perfectly reflecting wall the pressure must be everywhere the same and perpendicular to the wall, since no direction is privileged and the rays impinge from all sides with the same energy. Now, according to Maxwell, the normal component of the tension upon a surface element perpendicular to the  $X$ -axis is, per unit area,

$$X_x = \frac{1}{2}(d_x^2 - d_y^2 - d_z^2) + \frac{1}{2}(h_x^2 - h_y^2 - h_z^2),$$

where  $d_x, d_y, d_z, h_x, h_y, h_z$  are the components of the electric and the magnetic field intensities  $\mathbf{d}$  and  $\mathbf{h}$ .

The tension upon the wall will be the mean value of this

expression. Owing to the isotropy of the radiation the mean squares of the components are equal to each other,

$$\overline{d_x^2} = \overline{d_y^2} = \overline{d_z^2} = \frac{1}{3} \overline{\mathbf{d}^2},$$

and similarly for the magnetic components. And since the density of energy is  $U = \frac{1}{2}(\overline{\mathbf{d}^2} + \overline{\mathbf{h}^2})$ , we have

$$\overline{X_x} = -\frac{1}{6}(\overline{\mathbf{d}^2} + \overline{\mathbf{h}^2}) = -\frac{1}{3}U.$$

The negative sign of this tension means that there is a positive radiation *pressure*.

26, 3. The radiation pressure is exceedingly small. It was demonstrated experimentally by Lebedew and measured by Nichols and Hull.

27. In order to *derive Boltzmann's law*, we now return to the space filled with radiation, enclosed by perfectly reflecting walls and a piston, and containing a small piece  $M$  of a black body. This has, on the one hand, the office of preserving the character of the radiation within the space as black radiation, and forms, on the other hand, the only part of our system in contact with a heat reservoir, by means of which energy can be supplied to or withdrawn from the radiation.

We have compared this space with a space filled with gas. Let us dwell upon this comparison. We imagine the state to be determined by the temperature  $T$  and the volume  $v$ . For any given  $T$  and  $v$  the radiation within the enclosure will possess a certain energy  $\epsilon$ .

The heat supplied to the system through  $M$  will be found back, first, in an increase of the radiation energy if its temperature is raised; second, in the work done upon the piston if it be displaced outward; and, third, in the energy of the radiation which fills out the additional volume. The quantity of heat supplied is thus, by the first law of thermodynamics,

$$dQ = \frac{\partial \epsilon}{\partial T} dT + \frac{\partial \epsilon}{\partial v} dv + p dv.$$

Now, by the second law,  $dQ/T$  is a total differential, viz. the differential of entropy, so that

$$\frac{\partial \eta}{\partial T} = \frac{1}{T} \frac{\partial \epsilon}{\partial T} \quad \text{and} \quad \frac{\partial \eta}{\partial v} = \frac{1}{T} \left( \frac{\partial \epsilon}{\partial v} + p \right),$$

and since

$$\frac{\partial^2 \eta}{\partial T \partial v} = \frac{\partial^2 \eta}{\partial v \partial T},$$

we have

$$\frac{\partial \epsilon}{\partial v} = T \frac{\partial p}{\partial T} - p.$$

This result has general validity, for solid, liquid, and gaseous bodies. What can we learn from it about our system which consists of the aether filled with black radiation ?

The pressure  $p$  depends only on the temperature. When the volume is increased, while the temperature is kept constant, the density of energy and thus also the pressure will remain constant. The state of affairs is the same as with the pressure of a saturated vapour. When its volume is increased, but the temperature is kept constant, the liquid takes care that the pressure shall not vary. In our case the black particle  $M$  takes care that, through the required heat supply, the density of energy and the pressure shall remain constant.

We now see at once that, when at constant temperature the volume is increased, the increase of energy is just equal to the amount of radiation energy occupying the added volume. Thus

$$\frac{\partial \epsilon}{\partial v} = U.$$

Our equation now becomes

$$U = \frac{1}{3} T \frac{dU}{dT} - \frac{1}{3} U,$$

$$\frac{dU}{U} = 4 \frac{dT}{T},$$

$$\log U = 4 \log T + \text{integration constant},$$

or

$$U = m T^4.$$

This is *Boltzmann's law*.

28. The density of the black radiation is closely connected with the intensity of the radiation emitted by a black body. In fact, the body emits, per second, through an element  $d\sigma$  of its surface within a cone  $d\omega$  perpendicular to  $d\sigma$ , the energy

$$2d\sigma d\omega \int q dn,$$

and the density of black radiation is  $U = \frac{8\pi}{c} \int q dn$ .

Thus also *the intensity of emission of a black body is proportional to the fourth power of the absolute temperature*. This is the law which was already discovered empirically by Stefan for practically black radiation before Boltzmann gave its theoretical derivation.

The law was later more thoroughly investigated and confirmed by experiments. Originally, a plate covered with lampblack (Leslie), or platinum black, or  $\text{FeO}$ , served as a black body. Wien has shown how a perfectly black body can be realised. Any desired degree of blackness can be arrived at as follows. Take a cavity provided with a small aperture through which light and heat rays can penetrate. If of the incident rays no perceptible fraction can re-emerge, *the aperture* is to be considered as *perfectly black*. The walls of the cavity need not at all be black. If only the wall opposite the aperture does not throw back the rays directly, then an incident ray will as a rule, even with reflecting walls, never come out again, provided the aperture is small. Thus we can say that the aperture absorbs everything and is, therefore, perfectly black.

29. We have considered the system traversed by rays, *i.e.* the aether within reflecting walls, filled with radiation, and the black body  $M$ , as a thermodynamical system.

On these lines we now proceed, and are going to attribute a *temperature* also to the aether or, if one so prefers, to *the radiation*. It seems natural to say that the radiation has the same temperature as the black body with which it is in equilibrium.

We shall also speak of *the entropy of the aether* taken separately instead of thinking, as heretofore, only of the entropy of the whole system radiation-and-body  $M$ .

The quantity  $dQ$  of heat supplied can be split into two parts, one for the body  $M$ , and another which increases the radiant energy. We can take for  $M$  a particle as small as we please. Its contribution to the heat supply may then be neglected. We write, as before,

$$dQ = \frac{\partial \epsilon}{\partial v} dv + \frac{\partial \epsilon}{\partial T} dT + p dv,$$

where now  $\epsilon$  will be the energy of the radiation only, *i.e.*

$$\epsilon = mvT^4.$$

Consequently,

$$dQ = \frac{4}{3} m T^4 dv + 4 m v T^3 dT.$$

This divided by  $T$  is the increase of entropy, so that

$$d\eta = \frac{4}{3}mT^3dv + 4mvT^2dT,$$

whence

$$\eta = \frac{4}{3}mvT^3,$$

apart from an integration constant which is now of no importance for us. Later on (Art. 39) we shall find reasons for equating it to zero.

Thus *the entropy of a given volume of black radiation is proportional to the third power of the temperature.*

At equal temperatures the entropies are proportional to the volumes. Thus we may speak of *the entropy per unit volume*,

$$S = \frac{4}{3}mT^3.$$

30. In a non-reversible change the entropy will increase. As an example may be taken the analogue of the case of a gas which without doing work rushes into an empty space. Let us imagine a space within reflecting walls, divided into two parts by a partition which is impermeable to heat. Let one of these be free of radiation, and the other full of black radiation. If the partition is suddenly removed, the radiation spreads out without work from the volume  $v_1$  to  $v_2$ . The energy remains constant and, provided there is but a small black particle, the radiation remains black.

To see the behaviour of the entropy,  $T$  has to be eliminated and the entropy expressed in terms of the energy  $\epsilon$  and the volume  $v$ .

Now, the entropy is

$$\eta = \frac{4}{3}mvT^3,$$

and since

$$T^4 = \frac{\epsilon}{mv},$$

we have

$$\eta = \frac{4}{3}m^{\frac{1}{4}}v^{\frac{3}{4}}\epsilon^{\frac{3}{4}}.$$

Thus, if the volume increases, from  $v_1$  to  $v_2$ , while the energy remains constant, the entropy increases.

### III

#### WIEN'S LAW

31, 1. We have written (Art. 23) for the density of energy of black radiation

$$U = \int_0^{\infty} u dn$$

and have proved that  $U$  is proportional to  $T^4$ . But this does not tell us how the quantity  $u$ , which through  $u dn$  determines the density of radiation of the frequency interval  $(n, n + dn)$ , depends on  $n$  and  $T$ . We will now derive another, particularly beautiful, theoretical law which to a certain extent answers this question, namely, *Wien's law*,\* which asserts that

$$u = n^3 f\left(\frac{n}{T}\right).$$

31, 2. This law can be proved by thermodynamical considerations with the aid of some laws of the theory of light. Our proof will be based upon the assumption that *each pencil of rays has a certain entropy*. One might think that in the following presentation the concept of entropy is handled somewhat freely. We shall yet return to this question (in Art. 43), but meanwhile we shall suppose without much ado that the density of entropy

$$S = \frac{4}{3} m T^3,$$

related to rays of all directions and all frequencies, can be split by putting

$$S = \int_0^{\infty} s dn,$$

---

\* W. Wien, "Eine neue Beziehung der Strahlung schwarzer Körper zum zweiten Hauptsatz der Wärmetheorie", *Berlin Sitzungsberichte*, 1893, p. 55.



where  $sdn$  is the density of entropy for the interval  $dn$ . Thus  $s$  will correspond to  $u$ .

Let us take only those rays whose direction lies within the cone of aperture  $d\omega$ . For these the density of energy is

$$\frac{1}{4\pi} u dnd\omega.$$

Let to this correspond the density of entropy

$$\frac{1}{4\pi} s dnd\omega.$$

Therewith the concept of *the entropy of a pencil of rays* will be fixed. But we must always keep in mind that it is essential *not* to think of the pencil as consisting of *precisely parallel and strictly monochromatic rays*. The intervals  $d\omega$  and  $dn$  must necessarily be retained in our considerations.

Henceforth any pencil, specified by certain intervals  $d\omega$  and  $dn$  and a given density of energy, will also possess a certain entropy;  $s$  will be a function of  $u$  and  $n$ .

Likewise, the pencil will have a certain *temperature*. Here we go a step further and ascribe a certain temperature to the aether and also to a particular pencil, viz. the temperature of the black radiation of which the pencil, in proportion to its intensity and the intervals  $dn$ ,  $d\omega$ , can form a part. This will be made more clear presently.

32. In dealing with black radiation we can speak of *an equilibrium between the rays of different frequencies* therein contained, in much the same way as of the equilibrium between the different phases of a substance which can pass from one phase to another. It is true that in the pure aether the rays could not transform into each other, but the presence of the smallest black body makes this passage possible, and it does not cost us much to carry into our considerations a tiny piece of carbon which will serve as an intermediary in the energy exchange between different frequency intervals.

We now proceed to formulate the conditions for the equilibrium between different kinds of rays. The entropy will have to be a maximum, so that in a small virtual passage of the radiation from one frequency to another, at constant total energy, the variation of the entropy will be zero.

Let, for a frequency  $n$ , the energy density  $u$  vary by  $\delta u$ . Then the condition of equilibrium will be

$$\delta S = \int_0^\infty \frac{\partial s}{\partial u} \delta u dn = 0$$

under the supplementary condition

$$\delta U = \int_0^\infty \delta u dn = 0.$$

Since these conditions have to be satisfied for any virtual variations  $\delta u$  whatever,  $\partial s / \partial u$  must have the same value for all elements of the integral. This necessary condition is also sufficient. We thus have

$$\frac{\partial s}{\partial u} = C.$$

33. The quantity  $C$  has for each black radiation a certain value, the same for all frequencies. It can thus be only a function of the temperature. We can prove that it is the reciprocal of the temperature.

Suppose the temperature of the radiation is raised, by a supply of heat, from  $T$  to  $T + dT$ . Then

$$\frac{dS}{dT} = \int_0^\infty \frac{\partial s}{\partial u} \frac{\partial u}{\partial T} dn = C \int_0^\infty \frac{\partial u}{\partial T} dn = C \frac{dU}{dT}.$$

But since  $dS$  and  $dU$  are increments of the total entropy and energy,

$$\frac{dS}{dT} = \frac{1}{T} \frac{dU}{dT},$$

which follows also from the formulae  $U = mT^4$  and  $S = \frac{4}{3} mT^3$ .

Thus we have indeed

$$\frac{\partial s}{\partial u} = \frac{1}{T}.$$

This relation can also serve as the definition of *the temperature of a pencil*,

$$T = 1 / \left( \frac{\partial s}{\partial u} \right).$$

According to this point of view different *pencils of rays*, in black radiation, are *in equilibrium* with each other, if they have *the same temperature*.

All this seems reasonable and satisfactory. The possibility of speaking of the temperature of a pencil will be useful in the sequel.

34. We say that a given pencil, with the intervals  $d\omega$  and  $dn$  and the energy density  $u$ , has a certain entropy density  $s$ . The only question is, how does  $s$  depend on  $u$  and  $n$ ?

Suppose that a pencil can be changed adiabatically and reversibly into another pencil, having different  $u$  and  $n$ . This would enable us to find out something about the relation between  $s$ ,  $u$ , and  $n$ . Now, some such process is possible. It has been indicated by Wien. In fact, the pencil in question can be thrown back by a perfect mirror in motion.

Let us imagine a pencil of rays (Fig. 13), limited by a fore-and-aft wave front, of length  $l$  and cross-section  $S$ , and therefore of volume  $V = Sl$ . The rays should be neither parallel nor strictly monochromatic. Otherwise one could not speak of the temperature or the entropy of the pencil. Thus let there be allowed intervals,  $d\omega$  for the direction

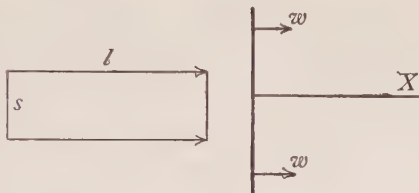


FIG. 13.

and  $dn$  for the frequency, and let the specification of the pencil be completed by prescribing the energy density  $u$ .

After the reflection all these quantities will be changed. Let the reflected pencil be characterised by the volume  $V'$  and by  $n'$ ,  $u'$ ,  $d\omega'$ ,  $dn'$ , and  $s'$ .

35, 1. The constancy of *entropy* can be written down at once.

The entropy per unit volume being  $\frac{1}{4\pi} s dn d\omega$ , we have, omitting the divisor  $4\pi$ ,

$$V's'd\omega'dn' = Vs d\omega dn.$$

35, 2. The *energy* of the pencil does not remain constant. It decreases by an amount equal to the work done by the radiation pressure upon the mirror. Here we are checked by a little difficulty, because the mirror moves, and we do not yet know what the pressure of light upon a moving mirror is like. But we can simplify the calculation by assuming the velocity  $w$  of

the mirror to be very small compared with the velocity  $c$  of light. The mirror will then, during the reflection, undergo but a small displacement, and in calculating the work we may neglect the small correction to be made in passing from the pressure for a fixed to that upon a yielding mirror.

Next, suppose that the pencil impinges normally upon the mirror and that both the radiation and the mirror move in the direction of the positive  $X$ -axis. By Art. 26, 1, the pressure per unit area will be twice the energy density of the incident pencil, *i.e.*  $\frac{1}{2\pi} u d\omega dn$ . The time during which this pressure acts is  $l/(c-w)$ , instead of which we may write  $l/c$ . Thus the work done upon the mirror is

$$\frac{1}{2\pi} u d\omega dn \frac{l}{c} w S,$$

and the energy equation, after the omission of the common factor  $1/4\pi$ ,

$$V' u' d\omega' dn' = V u d\omega dn - 2 V u d\omega dn \frac{w}{c}.$$

35, 3. Also *the frequency* must change. This variation could be written down by applying Doppler's principle. We prefer, however, to derive it by another method. The frequency of the reflected light depends also on the direction of incidence. In the present case we can write, for the incident ray,

$$d_y = a \cos n \left( t - \frac{x}{c} + p \right),$$

and for the reflected one,

$$d_y' = a' \cos n' \left( t + \frac{x}{c} + p \right).$$

At the surface of the mirror, *i.e.* for

$$x = wt,$$

there must hold, for all  $t$ , a certain relation between  $d_y$  and  $d_y'$ . This is possible only if the coefficients of  $t$  in the cosines are, for  $x = wt$ , the same. Thus,

$$n' \left( 1 + \frac{w}{c} \right) = n \left( 1 - \frac{w}{c} \right),$$

or, again, with the neglect of higher powers of  $w/c$  (which henceforth will be made without explicit mention),

$$n' = n \left( 1 - 2 \frac{w}{c} \right),$$

and therefore,

$$dn' = dn \left( 1 - 2 \frac{w}{c} \right).$$

35, 4. The *variation of the volume* is readily found by noticing that the cross-section of the pencil is not altered and that in the length of the pencil the same number of waves must be found after as before the reflection.  $V$  changes thus proportionally with the wave-length, so that

$$V'n' = Vn$$

and

$$V'dn' = Vdn.$$

35, 5. How does the *interval*  $d\omega$  change? Here a certain complication arises owing to the fact that the ordinary law of reflection is not applicable to the yielding mirror. A ray impinging under the angle  $\alpha$  can be represented by an expression in  $Y$  which occurs

$$\cos n \left( t - \frac{x \cos \alpha + y \sin \alpha}{c} + p \right).$$

Similarly, for the same ray after the reflection under the angle  $\alpha'$ ,

$$\cos n' \left( t + \frac{x \cos \alpha' - y \sin \alpha'}{c} + p' \right).$$

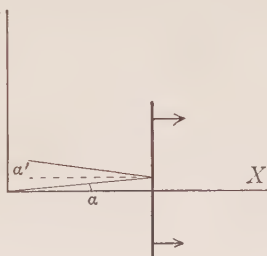


FIG. 14.

At the surface of the mirror, *i.e.* for  $x=wt$ , there must again be an agreement between the two cosines. Now, since  $\alpha$  and  $\alpha'$  are small, both  $\cos \alpha$  and  $\cos \alpha'$  are, with sufficient approximation, equal 1, and with regard to the coefficients of  $t$  we have the relation which has just been found (35, 3). The comparison of the coefficients of  $y$  gives

$$n \sin \alpha = n' \sin \alpha',$$

whence,  $\alpha$  and  $\alpha'$  being small and  $n' = n(1 - 2w/c)$ ,

$$\alpha' = \alpha \left( 1 + 2 \frac{w}{c} \right).$$

The aperture of the cone  $d\omega$  belonging to our pencil is proportional to the square of  $\alpha$ , so that

$$d\omega' = d\omega \left(1 + 4\frac{w}{c}\right).$$

36. Using these results we find at once from our energy and entropy equations

$$u' = u \left(1 - 6\frac{w}{c}\right)$$

and

$$s' = s \left(1 - 4\frac{w}{c}\right),$$

keeping in mind that  $n' = n(1 - 2w/c)$ . Incidentally we may note that our results would be exactly the same if instead of a yielding mirror one moving against the radiation had been taken.

We know that  $s$  is a function of  $u$  and  $n$  which has general validity, so that  $s'$  is the same function of  $u'$  and  $n'$ .

The factor  $(1 - 6w/c)$  can be considered as the third power of  $(1 - 2w/c)$ , which is the ratio of the frequencies.

Thus we find the *invariant*

$$\frac{u'}{n'^3} = \frac{u}{n^3},$$

and similarly,

$$\frac{s'}{n'^2} = \frac{s}{n^2}.$$

Now,  $s$  being a function of  $u$  and  $n$ , such that if  $u/n^3$  remains constant, this is also the case with  $s/n^2$ , one of these invariants must be a function of the other. In this way we find, as the required relation between  $s$ ,  $u$ , and  $n$ ,

$$\frac{s}{n^2} = F\left(\frac{u}{n^3}\right)$$

or

$$s = n^2 F\left(\frac{u}{n^3}\right).$$

37. In order to *introduce the temperature*, let us remember that, by definition,

$$\frac{\partial s}{\partial u} = \frac{1}{T}.$$

This, together with the expression just found for  $s$ , gives

$$\frac{1}{T} = \frac{1}{n} F'\left(\frac{u}{n^3}\right),$$



a formula which shows how the temperature of a given pencil is determined by its intensity ( $d\omega$  and  $dn$  being given). By inversion we find herefrom a formula showing how the intensity of a pencil depends on its temperature, viz.

$$u = n^3 f\left(\frac{n}{T}\right).$$

Wien's law is thus derived. The form of the function  $f$  remains still unknown, but the relation between  $u$ ,  $n$ , and  $T$  is in so far determined that we know  $u$  to be  $n^3$  times a function which depends only on the ratio  $n/T$ .

38. Wien's law can readily be put into the usual form in which it gives the distribution of energy over the different wave-lengths. In fact, put

$$n = \frac{2\pi c}{\lambda}.$$

Then to  $dn$  will correspond, in terms of the wave-length interval,  $\frac{2\pi c}{\lambda^2} d\lambda$ . The density of energy in an interval  $dn$  of the spectrum will thus be

$$u dn = \frac{2\pi c}{\lambda^2} u d\lambda = \Phi(\lambda, T) d\lambda.$$

Now, by Wien's law,

$$\Phi(\lambda, T) = \frac{2\pi c}{\lambda^2} n^3 f\left(\frac{n}{T}\right) = \frac{(2\pi c)^4}{\lambda^5} f\left(\frac{2\pi c}{\lambda T}\right)$$

or

$$\Phi(\lambda, T) = \frac{1}{\lambda^5} \psi(\lambda T),$$

which is the required form.

The significance of this formula is most conveniently explained by a graphical representation of the function  $\Phi$ , such as it was found experimentally by O. Lummer and E. Pringsheim.\*

If the curve representing  $\Phi$  as function of  $\lambda$  be given for a certain temperature  $T$ , say  $373^\circ$ , then, by Wien's law, it will be known also for any other temperature  $T'$ . Choose at the temperature  $T$  a given  $\lambda$ , and at the other temperature a wave-length  $\lambda'$ , such that  $\lambda' T' = \lambda T$ . Then  $\psi$  will be the same for the

\* "Die Strahlung eines schwarzen Körpers zwischen  $100$  und  $1300^\circ$  C.", *Ann. Phys. Chem.* lxxiii. p. 395, 1897; "Die Verteilung der Energie im Spektrum des schwarzen Körpers", *Verh. d. D. Phys. Ges.* i. p. 23, 1899.

wave-length  $\lambda'$  at the temperature  $T'$  as for  $\lambda$  at the temperature  $T$ . To find the ordinate  $\Phi$ , however, we have to divide  $\psi$  by  $\lambda'^5$ , i.e. to magnify the old ordinate in the ratio  $(\lambda/\lambda')^5$ .

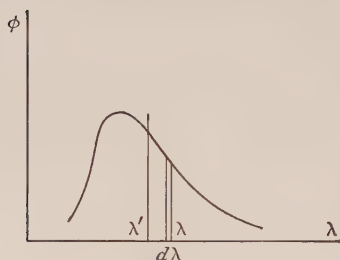


FIG. 15.

For the temperature  $T'$  we thus obtain a curve whose abscissae are  $T/T'$  times the abscissae and whose ordinates are  $(T'/T)^5$  times the ordinates of the original curve. Notice that the area under the curve is thus changed proportionally to  $T^4$ , which agrees with Boltzmann's

law. In fact, it will be readily seen that this area represents the total density of energy.

We can expect  $\psi$  to be an increasing function, since for a given wave-length the density of energy will certainly increase with the temperature. But the case is somewhat more intricate, if we ask for the variation of the density of energy with the wave-length at a fixed temperature. For, although  $\psi$  increases, the factor  $1/\lambda^5$  diminishes with increasing  $\lambda$ , and one understands that the density of energy may well have a maximum. Such, in fact, is, according to measurements, the case.

At each temperature the density of radiation attains at a certain wave-length  $\lambda_m$  a maximum, and it follows from Wien's law that, for different temperatures,

$$\lambda_m : \lambda'_m = T' : T,$$

i.e. the wave-lengths of maximum radiation are inversely proportional to the temperatures. With increasing temperature the energy is displaced towards the shorter waves. Whence the name of Wien's *displacement law*.

39. It is worth while to dwell yet on the formula

$$u = n^3 f\left(\frac{n}{T}\right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the inversion of

$$T = \frac{n}{F'\left(\frac{u}{n^3}\right)}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which we have derived from

$$s = n^2 F\left(\frac{u}{n^3}\right). \quad (3)$$

From these formulae follows again Boltzmann's law. In fact, introducing into the expression

$$U = \int_0^\infty u dn = \int_0^\infty n^3 f\left(\frac{n}{T}\right) dn,$$

the new variable  $\nu = n/T$ , one finds for the density of energy

$$U = T^4 \int_0^\infty \nu^3 f(\nu) d\nu = m T^4.$$

Similarly we find for the density of entropy, after some partial integrations,

$$S = \int_0^\infty s dn = \int_0^\infty n^2 F\left(\frac{u}{n^3}\right) dn = -\frac{1}{3} \int n^3 F'\left(\frac{u}{n^3}\right) \left\{ \frac{du}{n^3} - \frac{3u dn}{n^4} \right\},$$

which, by (2), becomes

$$-\frac{1}{3} \int \frac{n}{T} du + \int_0^\infty \frac{u dn}{T} = \frac{4}{3T} \int_0^\infty u dn = \frac{4}{3} m T^3,$$

if, in connection with the partial integrations, we may assume that

$$\lim_{n \rightarrow \infty} n^3 F\left(\frac{u}{n^3}\right) = 0 \quad \text{and} \quad \lim_{n \rightarrow \infty} nu = 0.$$

There is something peculiar about this entropy. It contains *no additive constant*. But, clearly, such also should be the case. In fact, let us imagine a vessel with perfectly reflecting walls, full of black radiation, shut off by a reflecting piston and containing a black body which takes care of the connection with a heat reservoir. Then, in a reversible isothermal expansion, the black body will give up heat to the radiation, viz. the equivalent of energy required to fill out the additional volume with radiation and to overcome the pressure of the piston. Now, this heat supply determines the increase  $dQ/T$  of entropy, which can be nothing else than the entropy of the radiation which fills out the volume increment.

40. As has already been remarked, the energy function  $u = n^3 f(n/T)$  increases with increasing temperature at constant wave-length. The function  $f(x)$ , therefore, decreases steadily with  $x$  increasing from 0 to  $\infty$ .

For the same reason, and since  $F'(u/n^3) = n/T$ ,  $F'(y)$  must be a decreasing function of  $y$  which remains, however, always positive from  $y=0$  to  $y=\infty$ . Its extreme values will be  $\infty$  and 0. Whence we see that  $F(y)$  will be expressed by a curve such

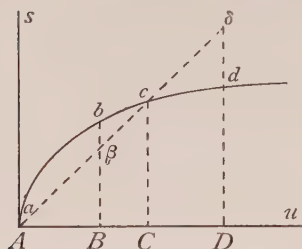


FIG. 16.

as that drawn in Fig. 16, which represents  $s$  as function of  $u$ . The curve has at  $u=0$  a vertical tangent, rises continually, turns its curved side away from the axis of abscissae, and becomes asymptotically horizontal. If we assume that in absence of radiation the entropy is nil (cf. the remark on the absence of an additive con-

stant), the function will vanish for  $u=0$ , so that the starting-point  $a$  of the curve will coincide with the origin.

41. These considerations lead to an interesting conclusion. Suppose that a *pencil of rays* of a certain colour is split by means of a thin plate into two parts, a *reflected* and a *transmitted* one. The energy of the incident pencil is, apart from the factor  $1/4\pi$ ,  $Vud\omega dn$ . It is easy to show that for the two partial beams  $Vd\omega dn$  is the same, but their energy densities,  $u_1$  and  $u_2$ , will differ from the original one. Of course

$$u = u_1 + u_2.$$

Similarly, the incident and the two partial beams will have different densities of entropy. Let the corresponding density functions be  $s$ ,  $s_1$ , and  $s_2$ . It can then be proved that

$$s < s_1 + s_2,$$

i.e. that the total entropy has increased.

In fact, let in Fig. 16, with  $u$  as abscissa and  $s$  as ordinate,  $AB = u_1$ ,  $AC = u_2$ , and  $AD = u_1 + u_2$ , so that  $CD = AB$ . Further, let  $Bb = s_1$ ,  $Cc = s_2$ , and  $Dd = s$ . Then it will be seen at once that only if the function  $s$  were linear along  $Ac\delta$  could we have

$$D\delta = Cc + B\beta.$$

We know, however, that  $s$  is represented by the solid curve, so that necessarily

$$Dd < Cc + Bb,$$

which proves the proposition.

In accordance with this increase of entropy such a *splitting into two pencils is an irreversible process*.

42. At first sight one might think that the splitting should be reversible. In fact, placing oneself on the standpoint of the electromagnetic theory of light, one might reason as follows:—

If Maxwell's equations for a transparent body are satisfied by

$$E_x = f_1(t, x, y, z), \quad E_y = f_2(t, x, y, z), \quad E_z = f_3(t, x, y, z),$$

$$H_x = g_1(t, x, y, z), \quad H_y = g_2(t, x, y, z), \quad H_z = g_3(t, x, y, z),$$

they will also be satisfied by

$$E'_x = f_1(-t, x, y, z), \quad E'_y = f_2(-t, x, y, z), \quad E'_z = f_3(-t, x, y, z),$$

$$H'_x = -g_1(-t, x, y, z), \quad H'_y = -g_2(-t, x, y, z), \quad H'_z = -g_3(-t, x, y, z).$$

In fact, it can be easily verified by substitution that, if the first set satisfies the fundamental equations, such as

$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = -\frac{1}{c} \frac{\partial B_x}{\partial t},$$

so also does the second set. ( $B_x, B_y, B_z$  are to be considered as homogeneous linear functions of  $H_x, H_y, H_z$ .)

But the change of  $t$  into  $-t$  means a reversal of the propagation. In fact, if the first set of field components represents a rectilinear pencil which is propagated in the direction  $\alpha, \beta, \gamma$ , say

$$E_x = a \cos n \left( t - \frac{x \cos \alpha + y \cos \beta + z \cos \gamma}{v} + p \right), \text{ etc.,}$$

then the second set,

$$\begin{aligned} E'_x &= a \cos n \left( -t - \frac{x \cos \alpha + y \cos \beta + z \cos \gamma}{v} + p \right) \\ &= a \cos n \left( t + \frac{x \cos \alpha + y \cos \beta + z \cos \gamma}{v} - p \right), \text{ etc.,} \end{aligned}$$

will represent a pencil with the opposite sense of propagation. This could also be confirmed by considering the corresponding Poynting vector which gives the flux of energy.

Moreover, those regions of space in which darkness prevailed in the first case will also be dark in the second case. All light rays are inverted in their direction, while their amplitude remains unaltered.

Our splitting should thus indeed be reversible, a result which in theoretical considerations can often be used.

But the contradictory results can in this case be reconciled by investigating more closely what should happen in order to bring about the inversion and recombination of the pencils. The incident pencil *a* and another, properly directed pencil *b* (Fig. 17) should co-operate in such a manner as to yield a single light pencil *c*.

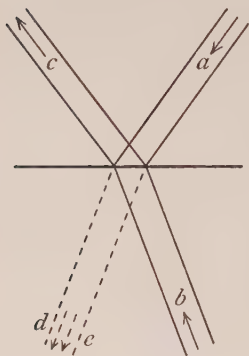


FIG. 17.

Now, the pencil *a* would by itself give rise to a pencil *d*, and *b* would as well contribute a reflected pencil *e*. The pencils *a* and *b* would thus not combine merely into *c*, unless the pencils *d* and *e* can be made to cancel each other. This, to be sure, is theoretically possible, if they are given the same amplitude and opposite phases. But then also *exactly* opposite phases.

Now, in the theory of radiation it is assumed that the spaces dealt with are large compared with the wave-length. Seeing, therefore, that in order to obtain the reversal by a re-reflection of the split pencil we have to work with such a high accuracy, we may safely say that the experiment is not feasible. But even if we succeeded in inverting the splitting of one ray by a delicate adjustment of the mirrors, this would not be a sufficient argument against our theory. For the pencils under investigation are always provided with a certain interval  $dn$  (cf. Art. 31, 2), so that an adjustment of the mirrors which would undo the splitting of one ray of the pencil, would not serve equally well the other rays.

43. The *irreversibility* of the splitting of a light pencil into two others can also be expressed in another way. In fact, for each of the partial pencils the temperature is lower than for the original one (cf. formula (2), Art. 39, and what has been said about  $F'$  in Art. 40). Thus *the energy has passed to a lower temperature*. Every scattering of the rays leads, then, to an increase of the entropy.

The inverse process, the combination of two pencils, would require the energy to pass to a higher temperature.

We have another instance of the increase of entropy, when a



light pencil is partially absorbed by a body which does not radiate itself and whose temperature is thus necessarily lower than that of the light ray. (Let us think, *e.g.*, of the absorption of the sun rays.) Also the temperature of the light ray falls. Consider a pencil  $Vd\omega dn$  which possesses the energy

$$\frac{1}{4\pi} V u d\omega dn.$$

Of this let an infinitesimal amount  $\nu$  be absorbed, the process not being accompanied by reflection. Then the entropy of the absorbing body will increase by  $\nu/T'$ , if  $T'$  be the temperature of the body. In the pencil,  $u$  changes by  $\delta u$ , so that

$$\frac{1}{4\pi} V d\omega dn \delta u = -\nu.$$

Consequently the entropy of the light pencil will undergo the change

$$\frac{1}{4\pi} \frac{\partial s}{\partial u} V d\omega dn \delta u = -\frac{\nu}{T},$$

and since  $T > T'$ , the total entropy will increase.

44. Before passing to consider the entropy of a polarised ray we may show, by way of introduction, how a ray can be made to penetrate from one into another medium without any appreciable reflection. Imagine the passage from the first medium, of refractive index  $n_1$ , to the second, of index  $n_2$ , brought about by a great number  $k$  of thin homogeneous layers whose indices have gradually increasing values, somewhat after the fashion of our atmosphere. Let the thickness of these layers, however, be large enough compared with the wave-length, to prevent interference phenomena.

For the passage from any of these layers to the following one, of relative refractive index  $n$ , hold the known formulae of Fresnel which give the ratios of the reflected to the incident amplitude for vibrations perpendicular to or in the plane of incidence, viz.

$$-\frac{\sin(i-r)}{\sin(i+r)} \text{ and } \frac{\tan(i-r)}{\tan(i+r)}$$

respectively. These ratios of the amplitudes tend for normal

incidence to  $-\frac{n-1}{n+1}$  and  $\frac{n-1}{n+1}$ . Consequently, the intensity of the reflected is to that of the transmitted light as  $\left(\frac{n-1}{n+2}\right)^2$  to  $\left(\frac{2\sqrt{n}}{n+1}\right)^2$ . If the refractivity,  $n-1=\delta$ , is very small, this ratio becomes  $\frac{1}{4}\delta^2$ , i.e. small of the second order.

Let each of the  $k$  layers have the same relative refractive index, viz.

$$n = \left(\frac{n_2}{n_1}\right)^{\frac{1}{k+1}} = 1 + \delta.$$

Of the light reflected upwards a certain fraction will again be reflected downwards, and so on. But these repeated reflections, giving rise to intensities of the order of  $\delta^4$ ,  $\delta^6$ , etc., can be entirely disregarded.

Thus the intensity of the light reflected upwards will be

$$I_r = I \cdot \frac{1}{4}\delta^2(k+1).*$$

Now, 
$$\log(1+\delta) = \frac{1}{k+1} \log \frac{n_2}{n_1}$$

or, approximately,

$$\delta = \frac{1}{k+1} \log \frac{n_2}{n_1},$$

and therefore,

$$I_r = I \left( \log \frac{n_2}{n_1} \right)^2 \cdot \frac{1}{4(k+1)}.$$

The greater  $k$ , the smaller the reflected fraction. Thus, if the transition is gradual and the thickness of the transition layers large compared with the wave-length, there will be no appreciable reflection.

45. If we now wish to make use of a doubly refracting medium in order to split a natural pencil of rays in two polarised ones, we can suppose that the transition on both sides of the medium takes place gradually. This fiction will help us to get rid of the reflection which would give us in addition an irreversible, and therefore undesirable splitting. *The splitting in two polarised pencils, obtained in such a way, is reversible.* The emergent rays can easily be sent back by means of mirrors. The recombination

[\*  $I$  being the transmitted intensity.]

of the two pencils into a single one does not now require any such delicate adjustment of the mirrors as was mentioned before. The case would be different if the light in the original pencil were not natural but already polarised, *e.g.* circularly, or rectilinearly, or elliptically. A recombination of the rays into circularly or rectilinearly polarised light would then again require such an accurate adjustment of mirrors, as to make a clean reversal of the splitting impracticable.

Also the splitting of a light pencil in two polarised ones by a pile of glass plates, upon which the rays impinge under the angle of polarisation, is reversible, provided that absorption in the pile is disregarded and that the transmitted pencil contains practically no rays whose vibrations are perpendicular to the plane of incidence.

46. It is clear that in a reversible splitting into polarised pencils the entropy remains unaltered. In either of the polarised pencils the energy density is one-half of the original one. Thus, the entropy function for a polarised pencil of energy density  $\frac{1}{2}u$  is

$$s' = \frac{1}{2}n^2F\left(\frac{u}{n^3}\right),$$

and therefore *the entropy function of a polarised pencil of energy density  $u'$ ,*

$$s' = \frac{1}{2}n^2F\left(\frac{2u'}{n^3}\right).$$

From the behaviour of the function  $F$ , as pointed out before, it can easily be concluded that *the entropy of the polarised pencil is smaller than that of a non-polarised one of equal intensity.*

This holds not only for rectilinearly polarised rays but, as can easily be shown, also for elliptically and circularly polarised light.

47. The entropy can be viewed in different ways. Thus, for instance, we can say that *the entropy is a measure of the disorder of the phenomena.* If in one portion of a gas all the molecules have at a certain instant a greater energy than in another, or if one half of the volume is filled with hydrogen and the other half with oxygen, then something will happen which will diminish this high degree of orderliness, and the entropy will rise.

Now, if we used up a certain amount of energy to make polarised rays with, there would be more order produced than in making ordinary rays. It is in full harmony with this that

polarised rays have a smaller entropy than non-polarised ones of the same energy.

The same can be said about the scattering, absorption, or other kinds of dissipation of radiant energy. In all these cases the disorder increases.

Let us still imagine that we have produced two pencils, both of the same energy and frequency, but of different volumes and different intervals  $d\omega$ ,  $dn$ , viz. that

$$\frac{1}{4\pi}uVd\omega dn = \frac{1}{4\pi}u'V'd\omega'dn',$$

but

$$V'd\omega'dn' > Vd\omega dn,$$

and therefore,

$$u' < u.$$

Now, it is true that in this case

$$s > s',$$

*i.e.* that the "smaller" pencil has the greater entropy density. Yet, owing to the repeatedly mentioned behaviour of the function  $s = n^2 F(u/n^3)$ , there will hold between the ratios of the entropy densities and the energy densities the inequality

$$\frac{s}{s'} < \frac{u}{u'},$$

so that ultimately the whole entropy will be greatest in that pencil in which the energy is least concentrated, that is to say, least condensed in volume or least crowded within the interval  $dn$  or  $d\omega$ .

If we make the pencil more and more homogeneous, *i.e.* the interval  $dn$  less and less, the entropy will be smaller and smaller.

But we cannot get rid of  $dn$ . Even the finest spectrum line has still some breadth.

## IV

### JEANS' FORMULA

48. GENERAL thermodynamical considerations have now carried us so far as to enable us to ascertain that the function  $u$ , which in

$$U = \int_0^{\infty} u dn$$

expresses the density of radiant energy belonging to the frequency interval  $dn$ , must have the form

$$u = n^3 f\left(\frac{n}{T}\right).$$

Further than this we cannot go, unless we enter more deeply upon the mechanism of the phenomena and are prepared to make with regard to it definite hypotheses enabling us to judge about the circumstances under which a stationary equilibrium between the energy emitted and that taken up by matter can be brought about. With the aid of certain assumptions, Planck succeeded in arriving at a formula by which the experimental facts are well represented. But before passing to his theory it will be well to expound the theory of Jeans,\* who, developing an idea due to Lord Rayleigh, bases himself upon general considerations of a different kind, in which an application is made of the theorem of equipartition of energy known from the kinetic theory of gases. Jeans' formula, however, holds only in the domain of great wave-lengths.

49. The theorem of *the equipartition of energy* is, in its nucleus, already contained in Maxwell's writings, where it is shown that a mixture of monatomic gases is in statistical equilibrium, if the mean kinetic energy of a molecule of each gas is the same, no matter

\* J. H. Jeans, "On the Partition of Energy between Matter and Aether", *Phil. Mag.* x. p. 91, 1905.

whether the molecules are left to themselves or are acted upon by conservative forces which can affect considerably the density distribution of the gases. The mean kinetic energy of a molecule is here proportional to the absolute temperature  $T$ .

This result was extended by Boltzmann, who drew also molecules consisting of two or more atoms into the circle of his statistical considerations. Each of these molecules can be assumed to form some system or other, which is capable of internal vibrations about a state of equilibrium and perhaps also of spinning. But this need not be specified. It will be enough to assume that each molecule has  $n$  degrees of freedom, so that its state is determined by  $n$  co-ordinates  $q_1, q_2, \dots, q_n$ , among which there may, *e.g.*, be those of the centre of gravity. Let these co-ordinates be so chosen that the kinetic energy of a molecule shall have the form

$$\frac{1}{2}(m_1\dot{q}_1^2 + m_2\dot{q}_2^2 + \dots + m_n\dot{q}_n^2).$$

Now, if the whole molecule takes part in the heat agitation, that is to say, if none of its degrees of freedom is withdrawn from the influence of the irregular interactions with other molecules, then, according to Boltzmann, to each degree of freedom of each molecule, and of each body, belongs the same mean kinetic energy which, moreover, is proportional to the absolute temperature. *To each degree of freedom belongs a mean kinetic energy*

$$\frac{1}{2}aT.$$

Thus, if a gas, consisting of  $N$  molecules, each of  $n$  degrees of freedom, is in contact with a large heat reservoir of temperature  $T$ , the *kinetic* energy contained in the gas, averaged over a long time, is  $\frac{1}{2}NnaT$ . If the number  $N$  is very great, the actual kinetic energy at a given instant differs so little from the mean value, that it can safely be represented by the same expression.

50. Jeans applies a consideration of the same kind to the aether. He assumes that, in energy exchanges, the share of *each degree of freedom of the aether in mean kinetic energy is  $\frac{1}{2}aT$* . This assumption, borrowed from statistical mechanics, takes here the place of a discussion on the manner in which a ponderable body and the aether act upon each other. In "equipartition"



one is concerned only with kinetic energy, while in the case of aether vibrations one has to do with electric and magnetic energy. In many cases, considerations about kinetic energy can be applied to magnetic energy, and electric energy can be taken as potential. This will also be done here. At the same time the idea readily suggests itself to consider our case as analogous to that of vibrating bodies, for which *the mean potential energy is equal to the kinetic one*.

To fix the ideas, take the aether contained in a rectangular parallelepipedon with perfectly reflecting walls. This will be a well-isolated system. For, since the walls are perfect conductors, the electric force will be everywhere normal to the wall, because the tangential component must be continuous at the boundary of two media and the electric force is nil inside a perfect conductor. But if the electric force is everywhere perpendicular to the wall, then the energy flux is, obviously, along the wall, so that no energy can pass outside or inside, and the system is, therefore, perfectly isolated.

In seeking the number of degrees of freedom of the aether we will take for it the number of modes in which the aether can vibrate. Namely, between the reflecting walls we can have standing vibrations [waves] as superpositions of progressive waves.

Now, if we ask how many modes of standing vibrations are possible, we see at once that there are infinitely many. In fact, with ever-decreasing wave-length there is no end to the number of possible vibrations. This, of course, is a great difficulty of the theory. For to an infinite number of degrees of freedom would correspond an infinite energy. Thus it comes that Jeans' formula, as already mentioned, holds only, as an approximation, for great wave-lengths.

51. Thus, in order to find the energy  $u dn$  for rays of frequencies contained between  $n$  and  $n + dn$ , we have to ask how many modes of standing waves with frequencies falling into this interval are possible in the aether between our reflecting walls.

Let three edges of the parallelepipedon coincide with the co-ordinate axes  $OX$ ,  $OY$ ,  $OZ$ , and let their lengths be  $q_1$ ,  $q_2$ ,  $q_3$ . A train of plane waves which proceeds in any direction given by the direction cosines  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  will be repeatedly reflected by the

walls, so that ultimately there will be eight different trains of plane waves crossing each other, with the direction cosines

$$\begin{aligned} & \mu_1, \quad \mu_2, \quad \mu_3 ; \\ -\mu_1, \quad \mu_2, \quad \mu_3 ; & \quad \mu_1, \quad -\mu_2, \quad \mu_3 ; \quad \mu_1, \quad \mu_2, \quad -\mu_3 ; \\ \mu_1, \quad -\mu_2, \quad -\mu_3 ; & \quad -\mu_1, \quad \mu_2, \quad -\mu_3 ; \quad -\mu_1, \quad -\mu_2, \quad \mu_3 ; \\ & -\mu_1, \quad -\mu_2, \quad -\mu_3. \end{aligned}$$

Let us write for the electric components in the first system of waves

$$d_x = fa \cos n \left( t - \frac{\mu_1 x + \mu_2 y + \mu_3 z}{c} + p \right),$$

$$d_y = ga \cos n\psi,$$

$$d_z = ha \cos n\psi,$$

where  $\psi$  is an abbreviation for the bracketed expression in the first formula,  $a$  the amplitude and  $f, g, h$  the direction cosines of the electric force, and  $p$  a phase constant. Similar expressions, with properly changed signs of the  $\mu$ 's, will hold for the remaining seven trains of waves. The constants to be chosen for the reflected trains of waves will be determined by the boundary conditions. Let us consider, for instance, the reflection which changes the first of the coefficients  $\mu_1, \mu_2, \mu_3$  into  $-\mu_1$ . This is a reflection at the  $YZ$ -plane or the opposite, parallel wall. Since the reflection is perfect, the amplitude  $a$  will, clearly, remain unaltered. There is also no discontinuity in the phase, so that  $p$  remains unaltered. Again, the vibrations are after the reflection still perpendicular to the direction of propagation, so that, *mutatis mutandis*, the relation

$$\mu_1 f + \mu_2 g + \mu_3 h = 0 \quad . \quad . \quad . \quad . \quad (a)$$

must continue to hold. Thus, if  $\mu_1$  is replaced by  $-\mu_1$ , then either  $f$  will be changed into  $-f$  or both  $g$  and  $h$  into  $-g$  and  $-h$ . But we have already seen that the electric force must be perpendicular to the wall, so that in the superposition of the incident and the reflected waves  $d_x$  only can survive. Consequently the second alternative must be chosen. Similar considerations applied to the remaining reflections will show that

the direction cosines of the electric force corresponding to the eight trains of waves are

$$\begin{aligned} & f, g, h; \\ & f, -g, -h; \quad -f, g, -h; \quad -f, -g, h; \\ & f, -g, -h; \quad -f, g, -h; \quad -f, -g, h; \\ & f, g, h. \end{aligned}$$

Thus, putting together all the wave trains, and adding each time the components  $d_x$ ,  $d_y$ ,  $d_z$  for two trains which are reflections of each other, we find ultimately

$$\begin{aligned} d_x &= -8fa \cos \frac{n\mu_1 x}{c} \sin \frac{n\mu_2 y}{c} \sin \frac{n\mu_3 z}{c} \cos n(t+p), \\ d_y &= -8ga \sin \frac{n\mu_1 x}{c} \cos \frac{n\mu_2 y}{c} \sin \frac{n\mu_3 z}{c} \cos n(t+p), \\ d_z &= -8ha \sin \frac{n\mu_1 x}{c} \sin \frac{n\mu_2 y}{c} \cos \frac{n\mu_3 z}{c} \cos n(t+p). \end{aligned}$$

The corresponding values of the magnetic components  $h_x$ ,  $h_y$ ,  $h_z$ , which can be derived from  $d_x$ ,  $d_y$ ,  $d_z$  by means of the field equations, are

$$\begin{aligned} h_x &= 8f'a \sin \frac{n\mu_1 x}{c} \cos \frac{n\mu_2 y}{c} \cos \frac{n\mu_3 z}{c} \sin n(t+p), \\ h_y &= 8g'a \cos \frac{n\mu_1 x}{c} \sin \frac{n\mu_2 y}{c} \cos \frac{n\mu_3 z}{c} \sin n(t+p), \\ h_z &= 8h'a \cos \frac{n\mu_1 x}{c} \cos \frac{n\mu_2 y}{c} \sin \frac{n\mu_3 z}{c} \sin n(t+p), \end{aligned}$$

where

$$f' = \mu_2 h - \mu_3 g; \quad g' = \mu_3 f - \mu_1 h; \quad h' = \mu_1 g - \mu_2 f. \quad (b)$$

These  $f'$ ,  $g'$ ,  $h'$  are constants determining a direction which is perpendicular to  $(\mu_1, \mu_2, \mu_3)$  as well as to  $(f, g, h)$ .

52. We see at once that these formulae express *standing waves*, since in the sines and cosines the co-ordinates  $x$ ,  $y$ ,  $z$  are separated from  $t$ , so that the electric force passes through zero or through its maximum in all points at the same instant. The nodes will be found where  $d_x$ ,  $d_y$ ,  $d_z$  vanish, i.e. on three systems of planes for which the cosine or the sine of  $n\mu_1 x/c$ , etc., is zero. Notice that, owing to the exchange of sin and cos, the magnetic field intensity has its maxima where the electric one is nil, and *vice versa*.

That the electric force is perpendicular to the walls is seen at once in the case of  $x=0$ ,  $y=0$ , and  $z=0$ . But this must hold also for the remaining faces of the parallelepipedon. For the plane  $x=q_1$ , for instance,  $d_y$  and  $d_z$ , and therefore also the sine which occurs in both of them, must vanish. Thus, a possible mode of standing vibrations must satisfy the conditions

$$\sin \frac{n\mu_1 q_1}{c} = 0, \quad \sin \frac{n\mu_2 q_2}{c} = 0, \quad \sin \frac{n\mu_3 q_3}{c} = 0,$$

or, if  $k_1, k_2, k_3$  are *integers*,

$$\frac{n\mu_1 q_1}{c} = k_1 \pi, \quad \frac{n\mu_2 q_2}{c} = k_2 \pi, \quad \frac{n\mu_3 q_3}{c} = k_3 \pi.$$

The numbers  $k_1, k_2, k_3$  must have the same signs as  $\mu_1, \mu_2, \mu_3$ . We may assume, without loss of generality, that they are *positive*. In fact, in the eight progressive wave trains which are compounded into the standing vibrations all possible combinations of positive and negative values of  $\mu_1, \mu_2, \mu_3$  occur, and there is nothing to prevent us from considering those waves for which all three values are positive as primary, *i.e.* producing by reflection all the other waves.

Since  $n/\pi c = 2/\lambda$ , the conditions for  $k_1, k_2, k_3$  may also be written

$$2\mu_1 q_1 = k_1 \lambda, \quad 2\mu_2 q_2 = k_2 \lambda, \quad 2\mu_3 q_3 = k_3 \lambda.$$

53. This gives us a great variety of standing waves. For  $k_1, k_2, k_3$  can be any three positive integers. If these be chosen, the corresponding wave-length will be found from the relation  $\mu_1^2 + \mu_2^2 + \mu_3^2 = 1$  or

$$\frac{k_1^2}{q_1^2} + \frac{k_2^2}{q_2^2} + \frac{k_3^2}{q_3^2} = \frac{4}{\lambda^2},$$

and  $\mu_1, \mu_2, \mu_3$  will be determined from the  $k$ 's and  $\lambda$  by means of the preceding three formulae.

Notice that, although after the choice of  $k_1, k_2, k_3$  the coefficients  $\mu_1, \mu_2, \mu_3$  are determined, different states of motion are still possible, since  $f, g, h$  remain to a certain extent arbitrary, having only to satisfy the condition of orthogonality to the direction  $\mu_1, \mu_2, \mu_3$ . But it will be readily seen that,  $\mu_1, \mu_2, \mu_3$  being fixed, there are only *two* modes of motion which can be considered as independent of each other. For one of these let  $f, g, h$  be so chosen as to satisfy the condition (a), Art. 51, and for

the other let  $f, g, h$  be replaced by the values  $f', g', h'$  determined by (b), Art. 51. If other modes of motion corresponding to the fixed values of  $\mu_1, \mu_2, \mu_3$ , and  $\lambda$  are still possible, they can be split into these two, and would thus give us nothing new.

54. To find the electro-magnetic energy for the case that a certain standing vibration is alone present, we have to extend the integral

$$\frac{1}{2} \int (\mathbf{d}^2 + \mathbf{h}^2) dS$$

over the volume of the parallelepipedon.

We can see at once that the mean value of the electric energy is equal to that of the magnetic energy. In fact, the expression to be integrated in either case contains squares of cosines and sines which, in view of the values of  $\mu_1, \mu_2, \mu_3$  and  $\lambda$  chosen in accordance with the boundary conditions, can be replaced, in the result of integration, by their mean value  $\frac{1}{2}$ . Again, the time average of  $\cos^2 n(t+p)$ , appearing in the electric energy, is equal to that of  $\sin^2 n(t+p)$  which occurs in the magnetic energy.

Next, if we have two different standing vibrations at the same time, the energy corresponding to their superposition is equal to the sum of the energies belonging to these vibrations taken separately. This is based upon the property that the integrals

$$\int (\mathbf{d} \cdot \mathbf{d}') dS \text{ and } \int (\mathbf{h} \cdot \mathbf{h}') dS$$

amount to nothing if  $\mathbf{d}, \mathbf{h}$  and  $\mathbf{d}', \mathbf{h}'$  represent two states to which correspond either mutually perpendicular vibrations ( $f, g, h$ ) and ( $f', g', h'$ ), at the same wave-length and direction of rays  $\mu_1, \mu_2, \mu_3$ , or different wave-lengths, or different directions of the rays. Thus we have

$$\int (\mathbf{d} + \mathbf{d}')^2 dS = \int [\mathbf{d}^2 + 2(\mathbf{d} \cdot \mathbf{d}') + \mathbf{d}'^2] dS = \int (\mathbf{d}^2 + \mathbf{d}'^2) dS,$$

and similarly for the integral of the magnetic energy.

55. Having thus ascertained that the energy for a complex state is the sum of the energies of the elementary modes of vibration, we can say that the latter are mutually independent and that to each state of motion characterised by given  $k_1, k_2, k_3$  and  $f, g, h$  belongs one degree of freedom. Applying, therefore, the theorem of equipartition we will assign to each of these

degrees of freedom the amount  $\frac{1}{3}aT$  of kinetic energy, and an equal amount of potential energy.

Consequently, to every set of values of  $k_1, k_2, k_3$ , to which correspond two modes of vibration, the amount  $\frac{4}{3}aT$  of mean energy will have to be attributed.

56. It remains only to determine *the number of sets of values of  $k_1, k_2, k_3$  for which the wave-length lies between  $\lambda$  and  $\lambda + d\lambda$ .*

To find this, let us first ask for the number of sets for which  $\lambda$  lies above a certain limit  $\lambda_0$ , for which, that is,

$$\frac{k_1^2}{q_1^2} + \frac{k_2^2}{q_2^2} + \frac{k_3^2}{q_3^2} < \frac{4}{\lambda_0^2}.$$

If this number be  $\phi(\lambda_0)$ , a function decreasing with increasing  $\lambda_0$ , then the number of sets corresponding to the wave-length interval  $\lambda_0$  to  $\lambda_0 + d\lambda_0$  will obviously be equal to the difference of the number of sets  $\phi(\lambda_0)$ , with  $\lambda$  above  $\lambda_0$ , and the number  $\phi(\lambda_0 + d\lambda_0)$ , with  $\lambda$  above  $\lambda_0 + d\lambda_0$ . The required number will thus be  $-\phi'(\lambda_0)d\lambda_0$ .

Consider for the moment the whole numbers  $k_1, k_2, k_3$  as the co-ordinates of a point. The problem is then reduced to finding the number of points within an ellipsoid of semi-axes

$$\frac{2q_1}{\lambda_0}, \quad \frac{2q_2}{\lambda_0}, \quad \frac{2q_3}{\lambda_0}.$$

The wave-length being [by assumption] small compared with the dimensions  $q$  of the parallelepipedon, this ellipsoid will be quite large. The points  $k_1, k_2, k_3$  are points of a cubic space lattice with the length unit as cube edge. The number of points contained in this large ellipsoid can thus be confounded with the number expressing its volume. But since we are concerned only with positive values of  $k_1, k_2, k_3$ , we have to take only an octant of this ellipsoid. Thus,

$$\phi(\lambda_0) = \frac{1}{8} \cdot \frac{4}{3} \pi \frac{8q_1q_2q_3}{\lambda_0^3} = \frac{4\pi}{3} \frac{q_1q_2q_3}{\lambda_0^3}.$$

Consequently, the number of sets  $k_1, k_2, k_3$  which give a vibration mode of wave-length contained between  $\lambda_0$  and  $\lambda_0 + d\lambda_0$  becomes

$$4\pi \frac{q_1q_2q_3}{\lambda_0^4} d\lambda_0.$$

In the equipartition of kinetic and potential energy each of these sets, to which belong two modes of vibration, has to receive



in all the energy  $\frac{4}{3}\alpha T$ . Thus we find for the energy in our aether parallelepipedon, corresponding to the wave-length interval  $d\lambda$ ,

$$\frac{16\pi}{3}\alpha T \frac{q_1 q_2 q_3}{\lambda^4} d\lambda,$$

i.e., per unit volume,

$$\frac{16\pi}{3} \frac{\alpha T}{\lambda^4} d\lambda,$$

or also, with  $\lambda = \frac{2\pi c}{n}$ ,  $|d\lambda| = \frac{2\pi c}{n^2} |dn|$ , in accordance with our notation,

$$u dn = \frac{2\alpha T}{3\pi^2 c^3} n^2 dn,$$

which is Jeans' formula.

57. This formula is undoubtedly correct for tolerably long waves. For this case it can also be deduced by another method.\* For short waves, however, it fails. In fact, according to this formula  $u$  would rise indefinitely with increasing frequency. The total energy of radiation would, at a given finite temperature, be infinitely great if the short waves therein contained could assert themselves so strongly. Besides, it has already been pointed out in deducing the formula that, if short waves were admitted, one would find infinitely many degrees of freedom. If a body possessing a finite energy were introduced into a portion of the aether enclosed by perfectly reflecting walls, then, according to this theory, all its energy would go over to the aether, since this would have infinitely many degrees of freedom. Each degree of freedom would then get next to nothing, so that the temperature of the aether would always remain exceedingly low.

Such is not at all the case. In reality  $u$  attains a maximum, as has already been mentioned. At high frequencies the energy density decreases again.

\* Cf. Lorentz, *Theory of Electrons*, chap. ii.

## V

### PLANCK'S FORMULA

58. We are now ready to pass to Planck's theory.\* Planck supposes that the exchange of energy between matter and aether is brought about by the intermediacy of particles in which electrical oscillations can take place. Such an idea naturally suggested itself. In fact, according to modern views, only charged matter can produce radiation or absorb it. The indispensable intermediaries ought to be found in vibrating electrons.

Planck calls the particles capable of electrical oscillations *resonators* and assumes that each of these resonators can vibrate only with a given natural frequency. Therein lies, no doubt, a certain limitation. Further, Planck assumes that the resonators are linear, *i.e.* that they have but one degree of freedom.

When such a resonator vibrates, its energy, averaged over a period, is half kinetic and half potential. According to the theorem of equipartition it would receive, in disordered heat agitation, the kinetic energy  $\frac{1}{2}aT$ ; its total share of energy  $\epsilon$ , would thus amount to  $\frac{2}{3}aT$ . We have seen in the last chapter that, in equipartition, the aether gets per unit volume, and in so far as radiation of the frequency interval  $dn$  is concerned, the amount of energy

$$udn = \frac{2aT}{3\pi^2c^3}n^2dn.$$

We shall adhere to the idea that, if there is to be a connection between the density of the field energy  $udn$ , taken for the frequency  $n$ , and the mean energy of a resonator of the same natural frequency, this connection should be governed by *equipartition* of the kinetic energy between *the resonator* and the isochronous

\* *Vorlesungen über die Theorie der Wärmestrahlung*, Leipzig, 1st ed., 1906; 5th ed., 1923; *Acht Vorlesungen über theoretische Physik*, Leipzig, 1910.

degrees of freedom of *the aether*, and thus, in accordance with the preceding formula, will be given by

$$u = \frac{n^2}{\pi^2 c^3} \epsilon_r.$$

This relation, then, we will retain. But in doing so we are forced to admit that  $\epsilon_r$  can no longer be equal to  $\frac{2}{3}aT$ . We must *sacrifice equipartition* in so far as interactions *between ponderable matter and the resonators* are concerned, although we shall retain it for the action between the resonators and the aether.

59. Planck arrives at the formula for his resonator by another method, basing himself upon the known laws of electrodynamics.

Instead of repeating here his derivation, we will abbreviate and simplify it by supposing that a resonator consists of an electron which is bound quasi-elastically to a position of equilibrium and which can move only in one direction, that of the  $X$ -axis, say. As is known from the electron theory, the vibrating electron, owing to its radiation, experiences an apparent resistance which is proportional to its velocity. If  $g$  be the coefficient of resistance,  $m$  and  $e$  the mass and the charge of the electron, further,  $x$  its displacement along the  $X$ -axis and  $-fx$  the quasi-elastic force, the equation of motion will be

$$m\ddot{x} + g\dot{x} + fx = ed_x,$$

where  $d_x$  is the  $X$ -component of the electric field intensity  $\mathbf{d}$ . If the vector  $\mathbf{d}$  belongs to a train of plane waves of (amplitude  $a$  and) frequency  $n$ , the equation will be satisfied by a function representing periodic oscillations of the same frequency  $n$ . If  $x$  and  $d_x$  be expressed by the real parts of  $pe^{int}$  and  $a_x e^{int}$ , then

$$p(-mn^2 + ign + f)e^{int} = ea_x e^{int}.$$

If  $a_x$  is real,  $p$  will be complex. This means that the phase of the excited vibrations differs from that of the waves. To find the mean energy of the vibrating electron we require only the amplitude, which is equal to the modulus of  $p$ . In fact, the mean total energy is

$$\frac{1}{2}f|p|^2 = \frac{1}{2}fe^2 \frac{a_x^2}{(f - mn^2)^2 + n^2g^2},$$

the square of the modulus of  $p$  being here expressed by the product of  $p$  into its conjugate.

In the radiation field all kinds of trains of waves run through

each other. These are completely incoherent, that is to say, there is not the least connection between their phases. But although the vibration of the electron produced by the co-operation of all these waves is pretty complicated, its mean energy can be put equal to the sum of the mean energies of the vibrations of the electron which would be excited by each train of waves taken separately.

To arrive first at the sum of the energies due to the action of the waves of frequency  $n$  to  $n + dn$ , we can take for the sum of the squares  $a_x^2$  twice the mean square of  $d_x$  or two-thirds of the mean square of the field intensity  $\mathbf{d}$  itself (cf. p. 232), as contributed by these waves. In terms of the energy density of the waves this sum will be  $\frac{2}{3}u_n dn$ .\* The further summation amounts then to an integration, and we have

$$\epsilon_r = \frac{1}{3}fe^2 \int_0^\infty \frac{u_n dn}{m^2(n_0^2 - n^2)^2 + n^2 g^2},$$

where  $n_0 = \sqrt{f/m}$  is the frequency of the free vibrations of the resonator.

As in Planck's own investigation, the possibility of carrying out this integration, even approximately, is conditioned by the circumstance that the coefficient of resistance  $g$  is exceedingly small. This coefficient determines the damping of the free vibrations of the resonator. It is a known fact that the smaller the damping, the narrower the interval into which must fall the frequency of the impressed forces, in order that these may excite a vibration comparable in intensity with that which would be attained at perfect resonance. Our resonator with its weak damping can thus be considered as sensitive only to the action of rays whose frequency differs very little from  $n_0$ .

The function to be integrated has thus at  $n = n_0$  such a sharp maximum that in all factors, except  $(n - n_0)$ ,  $n$  can practically be replaced by  $n_0$ . This simplification gives

$$\epsilon_r = \frac{1}{3}fe^2 u_{n_0} \int_0^\infty \frac{dn}{4m^2 n_0^2 (n - n_0)^2 + n_0^2 g^2}.$$

Introducing the new integration variable

$$y = 2 \frac{m}{g} (n - n_0)$$

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\* The subscript  $n$  has been added to avoid a possible misunderstanding. It will remind us that the function  $u$  is to be taken for the argument  $n$ .

and replacing the lower integration limit, which for  $y$  is a large negative number, by  $-\infty$ , one finds

$$\epsilon_r = \frac{1}{6} \frac{f e^2 n_{n_0}}{m n_0^2 g} \int_{-\infty}^{+\infty} \frac{dy}{1+y^2}.$$

The integral is arc tan  $y$  and, taken between its limits, gives  $\pi$ . Again,  $n_0^2$  cancels with  $f/m$ , and the value of  $g$  for vibrations of frequency  $n_0$  being

$$g = n_0^2 \frac{c^2}{6\pi c^3},$$

we arrive at the result

$$\epsilon_r = \frac{\pi^2 c^3}{n_0^2} u_{n_0},$$

in which we recognise the previously given relation between the mean energy of a resonator and the energy density of radiation in unison with it.

60. We will now leave the aether on one side and consider the distribution of energy between the atoms, whose share in kinetic energy is  $aT$ , and the resonators. Here we shall be guided by two ideas which Planck introduces as *auxiliary assumptions*.

The first of these is that of all possible distributions of the energy between the atoms and the resonators in reality that will take place which is, or at least can be called the "*most probable*" one.

The second assumption is that, while an atom or a molecule can change their velocity and thus acquire or give up energy in a perfectly continuous manner, the resonators can take up energy only in *definite amounts* [*quanta*]. Their energy can only increase or decrease by certain quantities, about which Planck had to assume that they are *proportional to the frequencies* (cf. Art. 65).

Nobody has yet succeeded in finding out what the mechanism should be like in order to bring about such a state of things.

61. Let us suppose that we have to do with two kinds of "elements,"  $n_1$  of the first and  $n_2$  of the second kind, which have the peculiarity that they can acquire and give up energy only in certain amounts which may be called *energy units*, viz.  $\epsilon_1$  for the first, and  $\epsilon_2$  for the second kind. Later on the elements of the

first kind will be identified with molecules or atoms, so that the amount  $\epsilon_1$  will have to be made infinitely small.

Let the total energy be  $E$ , of which the elements of the first kind have, in all,  $p_1$  units, and those of the second kind  $p_2$  units, so that

$$p_1\epsilon_1 + p_2\epsilon_2 = E. \quad . \quad . \quad . \quad (1)$$

It is clear that,  $E$  being given,  $p_1$  and  $p_2$  can still vary. In other words, different distributions are possible. To fix the ideas we will assume that the units  $\epsilon_1$  and  $\epsilon_2$  are commensurable. There can be no objection to this. Let us, then, put

$$\epsilon_1 : \epsilon_2 = q_1 : q_2,$$

where  $q_1$  and  $q_2$  are co-prime integers. Without such an assumption it might happen that in some energy distributions a remainder would be left over.

Let  $p_1$  be the smallest value of  $p_1$  which satisfies the equation (1). To this corresponds  $p_2$ , the greatest value of  $p_2$ . We then have a whole series of possible values of  $p_1$  and  $p_2$ ,

|               |               |
|---------------|---------------|
| $p_1,$        | $p_2,$        |
| $p_1 + q_2,$  | $p_2 - q_1$   |
| $p_1 + 2q_2,$ | $p_2 - 2q_1$  |
| $p_1 + 3q_2,$ | $p_2 - 3q_1,$ |
| etc.          | etc.          |

Let us now assume that the number of terms of these series is very great. Such will be the case if  $p_2$  is great compared with  $q_1$  or the total energy  $E$  great compared with  $q_1\epsilon_2$ . Also the numbers  $n_1$  and  $n_2$  of the elements will be assumed to be great numbers.

If the partition of  $E$  into  $p_1$  units of the first and  $p_2$  units of the second kind be fixed, the  $p_1$  units ( $\epsilon_1$ ) of energy can still be distributed among the elements of the first kind in very many different ways, and with each of these a similarly great number of possible distributions of the  $p_2$  units over the  $n_2$  elements of the second kind has to be combined. There is thus, for each choice of  $p_1$  and  $p_2$ , still a great number  $s$  of possible distributions.

Planck calls that partition into  $p_1$  units of the first and  $p_2$  units of the second kind *the most probable one, for which the number  $[s]$  of possible distributions is greatest*. This becomes quite



reasonable if to such a partition belongs a value of  $s$  which is much in excess of the others.

62. In how many ways can  $p$  units be distributed among  $n$  elements? If, for each of the distributed units, we note the number of the element in which it has been placed, we get an assemblage or, we may say, a combination of  $p$  numbers. Since an element can receive more than one unit, it may happen that in the combination of  $p$  element numbers the same number occurs more than once. Thus we see that the number of possible distributions of  $p$  units among  $n$  elements is equal to the number of combinations of  $n$  elements  $p$  by  $p$  with repetitions, as known from combinatorial algebra, *i.e.*

$$\frac{(n+p-1)!}{(n-1)! p!}$$

Hence the distribution of the  $p_1$  and  $p_2$  units of energy among the two kinds of elements can be accomplished in

$$s = \frac{(n_1+p_1-1)!}{(n_1-1)! p_1!} \cdot \frac{(n_2+p_2-1)!}{(n_2-1)! p_2!}$$

different ways. This number is therefore a measure of the probability of a partition determined by  $p_1$  and  $p_2$ . For what set of values of  $p_1$  and  $p_2$  does it attain its maximum?

To answer this question, let us pass from a certain set to the following one. Then since  $p_1$  increases by  $q_2$  and  $p_2$  decreases by  $q_1$ , the expression for  $s$  will be multiplied by the factor

$$\frac{(n_1+p_1)(n_1+p_1+1) \dots (n_1+p_1+q_2-1) \cdot (p_2-q_1+1) \dots p_2}{(p_1+1) \dots (p_1+q_2) \cdot (n_2+p_2-q_1) \dots (n_2+p_2-1)}.$$

Now, running through the series of the different partitions we will see that this factor is at first greater than 1 and ultimately becomes smaller than 1. Hence the set  $p_1, p_2$  for which  $s$  attains a maximum must give for this factor the value 1.

We have already assumed that the  $p$ 's and the  $n$ 's are great numbers, and much greater than the  $q$ 's. Such being the case, we may as well put  $p_1$  and  $p_2$  in place of  $p_1+q_2$  and  $p_2-q_1$ , and thus replace the four groups of factors in the last expression by powers of  $n_1+p_1, p_2, p_1$ , and  $n_2+p_2$ . This is so much as to say that we need not inquire which distribution gives just the greatest value of  $s$ . We may as well be content with one of the neighbour distributions.

We thus have to find  $p_1$  and  $p_2$ , such that

$$\frac{(n_1 + p_1)^{q_2}}{p_1^{q_2}} \cdot \frac{p_2^{q_1}}{(n_2 + p_2)^{q_1}} = 1.$$

This condition could also be arrived at by applying Stirling's approximate formula to the factorials appearing in the expression for  $s$ .

The last formula can be written

$$\left(1 + \frac{n_1}{p_1}\right)^{q_2} = \left(1 + \frac{n_2}{p_2}\right)^{q_1},$$

or, since  $q_1$  and  $q_2$  are proportional to  $\epsilon_1$  and  $\epsilon_2$ ,

$$\left(1 + \frac{n_1}{p_1}\right)^{1/\epsilon_1} = \left(1 + \frac{n_2}{p_2}\right)^{1/\epsilon_2} \quad \dots \quad (2)$$

This equation, together with (1), Art. 61, will give us  $p_1$  and  $p_2$ .

63. The equation (2) expresses the condition for *the most probable distribution* or, by our assumption, for the distribution in stationary equilibrium, in a very handy form: an expression related to the system of elements of the first kind is equal to one related only to the other system. Whence we see that, if one more system were in play, consisting of  $n_3$  elements of a third kind which would receive  $p_3$  energy units  $\epsilon_3$ , also the expression

$$\left(1 + \frac{n_3}{p_3}\right)^{1/\epsilon_3}$$

would have to be equal, in a stationary equilibrium, to the two others. Consequently that expression will, *for all kinds* of elements, be equal to one and the same constant, to which we may give an exponential form. Thus,

$$\left(1 + \frac{n}{p}\right)^{1/\epsilon} = e^{C'},$$

whence

$$\frac{p}{n} = \frac{1}{e^{C'\epsilon} - 1}.$$

64. The *mean energy* of an element will now evidently become

$$\frac{\epsilon}{e^{C'\epsilon} - 1},$$

where  $C$  is always positive. The value of this constant can be found from the energy equation (1),

$$p_1\epsilon_1 + p_2\epsilon_2 = E,$$

which now becomes

$$\frac{n_1 \epsilon_1}{e^{C\epsilon_1} - 1} + \frac{n_2 \epsilon_2}{e^{C\epsilon_2} - 1} = E.$$

Notice that the value just found for the mean energy of each element depends on the size of  $\epsilon$ , that is to say, on the size of the energy units which it can take up or give out. The greater  $\epsilon$  the smaller the mean energy of an element. In fact, differentiating the expression for the mean energy with respect to  $\epsilon$ , we get

$$\frac{e^{C\epsilon} - 1 - C\epsilon e^{C\epsilon}}{(e^{C\epsilon} - 1)^2},$$

which is always negative, as will be seen by developing the exponential functions of the numerator into series and noticing that the second and higher powers of  $\epsilon$  due to the last term have negative coefficients of greater absolute value than those of equal powers due to the first term.\*

We thus see that the things which crave only for large portions of energy get on the average the least of it.

65. The result found above can now be applied to the resonators and to the atoms of ordinary matter with which they can interact. We will assume that the atoms can absorb or give up energy in infinitely small amounts. For the resonators Planck assumes  $\epsilon = h\nu$ , where  $\nu$  is the frequency per second (so that our frequency  $n$  is  $2\pi\nu$ ).

We shall deviate somewhat from Planck. On the one hand, we will take away one *translational degree of freedom from a molecule* [or atom] and, on the other hand, we will count a *resonator*, which can acquire potential as well as kinetic energy, as *two elements*, each of which can receive or give up energy in amounts equal to  $\frac{1}{2}h\nu$ .

The mean energy of a molecule per degree of freedom, to be attained by letting  $\epsilon$  tend to zero, will be

$$\lim_{\epsilon \rightarrow 0} \frac{\epsilon}{e^{C\epsilon} - 1} = \lim_{\epsilon \rightarrow 0} \frac{\epsilon}{C\epsilon} = \frac{1}{C},$$

so that

$$\frac{1}{C} = \frac{1}{2}kT,$$

if, as in Planck's notation,  $\frac{3}{2}kT$  stands for the mean kinetic energy of a gas molecule. Thus  $\bar{C} = 2/kT$ .

\* [As e.g.  $-C^2\epsilon^2$  against  $+\frac{1}{2}C^2\epsilon^2$ ,  $-\frac{1}{2}C^3\epsilon^3$  against  $\frac{1}{6}C^3\epsilon^3$ , and so on, while the first powers of  $\epsilon$  cancel.]

The mean kinetic energy of the resonator will now become

$$\frac{\frac{1}{2}h\nu}{e^{\frac{1}{2}h\nu/C} - 1},$$

and therefore, *the mean total energy of the resonator,*

$$\epsilon_r = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

To mention it once more, we are unable to indicate any mechanism which would bring about such a state of affairs, viz. that in interactions energy may pass to the resonators in certain amounts only. The laws which would necessitate this lie entirely in the dark. The classical laws of mechanics and electrodynamics are utterly inadequate to force upon the resonators such a behaviour.

66. Let us now return to the formula which correlated the density of radiation with the mean energy of a resonator,

$$u = \frac{n^2}{\pi^2 c^3} \epsilon_r.$$

Substituting here the value just found for  $\epsilon_r$ , we have

$$u dn = \frac{n^2}{\pi^2 c^3} \frac{h\nu}{e^{h\nu/kT} - 1} dn,$$

or, introducing  $\nu$  throughout,

$$u d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}.$$

This is *Planck's formula* which agrees well with Lummer and Pringsheim's and Rubens and Michel's measurements.

We see that for long waves it reduces to Jeans' formula. For we then reach the domain of small frequencies, and the energy portions for the resonators become small, so that we approach the case in which the resonators would behave with respect to energy exchanges like gas molecules and the theorem of equipartition would hold. Here, therefore, Jeans' formula comes to its rights.

For any wave-length, Planck's formula satisfies the requirements expressed by Wien's displacement law, and this, together with its property of yielding for indefinitely decreasing wave-lengths an energy unit which rapidly tends to zero, prevents it also from infringing against Boltzmann's law. That it satisfies

the displacement law is due to the circumstance that the energy units for the resonators have been assumed to be proportional to their frequency.

67. By comparing his formula with the observations Planck has derived the values of  $h$  and  $k$ . He found

$$h = 6.415 \cdot 10^{-27} \text{ erg sec.}$$

and

$$k = 1.346 \cdot 10^{-16} \text{ erg/degree.}$$

The reason why the value of  $k$  is of so much importance is that it serves as the key to the knowledge of a number of other universal constants. In the first place it helps us to determine the so-called constant of Avogadro, *i.e.* the number of molecules contained in a gram molecule of a substance. If this number be denoted by  $N$ , the total kinetic energy of translation of the molecules of an ideal gas at the temperature  $T$  is, per gram molecule,  $\frac{3}{2}NkT$ . By the kinetic theory of gases this is one and a half times the product of the pressure into the volume which, on the other hand, is given by the formula

$$pV = RT,$$

where  $R$ , the gas constant for a gram molecule, is known from measurements on gases.\* Thus, since

$$R = Nk,$$

the value of  $N$  can be found if that of  $k$  be known.

In its turn Avogadro's number enables us to determine the charge carried by the ions in electrolytic solutions. In fact, the total amount of charge carried by the ions of a gram atom, *e.g.* of silver, is well known.† Dividing this by  $N$ , we find the elementary charge  $e$ , which is also the charge carried by the (negative) electrons. Again, since the ratio  $e/m$  of the charge of an electron to its mass (for small velocities) has been determined,‡ we come also to know the mass of an electron.

68. The constant  $h$  is an entirely new universal constant. As will be seen from its value just quoted, it has the dimensions of an energy multiplied by a time or of what in mechanics is called action. This can be verified at once by noticing that  $h\nu$

\* At  $0^\circ \text{ C.}$  ( $273.11^\circ \text{ abs.}$ ) and 76 cm. mercury (1,013,700 dynes per  $\text{cm.}^2$ ) the volume of a gram molecule is 22,412  $\text{cm.}^3$ . Whence,  $R = 1,013,700 \times 22,412/273.11$ .

† This charge, the farad, amounts to 9649.4 electromagnetic units.

‡ According to Bucherer,  $e/m = 1.767 \cdot 10^7$  electromagnetic units per gram.

is a quantum of energy and the frequency  $\nu$  the reciprocal of a vibration period. The constant  $h$  is, therefore, called Planck's *elementary quantum of action*.

The fundamental importance of this constant lies in the applicability of the quantum hypothesis to several other domains. We cannot enter here upon these applications.\* To give only an example we may mention Einstein's experimentally confirmed theory of the photo-electric effect, which amounts to stating that the electrons liberated from the surface of a metal by the action of light cannot have a greater kinetic energy than that equivalent to a quantum  $h\nu$  corresponding to the frequency of the incident light. The inverse of this in a certain sense is what Duane and Hunt found about the wave-length of X-rays which can be excited by bombarding the antikathode with electrons: the frequency of the X-rays has an upper limit which is fixed by the condition that the energy quanta  $h\nu$  in the X-radiation cannot be greater than the kinetic energy of the electrons which gave rise to the radiation.

Bohr has applied the quantum hypothesis to Rutherford's model of the atom.† This has been a most lucky idea of the Danish physicist, which enabled him not only to account for the series of spectrum lines of hydrogen and [ionised] helium but to disclose at the same time a striking connection between Rydberg's spectroscopic constant appearing in the series and the constants  $e$ ,  $h$ , and  $e/m$ .

We must be content with these few remarks and refer the student for further details to the literature given below.

69. The values found for Avogadro's number and the charge of an electron by means of Planck's value of  $h$  can be compared with the values arrived at by other investigators, as *e.g.* with the number  $N$  calculated by Perrin from his experiments on the Brownian movement of suspended particles or with the value of  $e$  obtained by Rutherford as the result of counting a large number of  $\alpha$ -particles and measuring their total charge. The agreement is very satisfactory. We will not list here all the numbers given by different investigators, but will quote only the values obtained by R. A. Millikan‡ from his accurate investigations on the charge

\* Cf. the following course of lectures on "The Theory of Quanta".

† N. Bohr, *Phil. Mag.*, xxvi. pp. 1, 476, 857; 1913.

‡ R. A. Millikan, "A New Determination of  $e$ ,  $N$ , and Related Constants", *Phil. Mag.*, xxxiv. p. 1, 1917. .



of floating oil droplets—results which impress one as very reliable. Millikan's values, with their mean errors, are :—

*Charge of an electron* . . . . .  $e = (4.774 \pm 0.005) \cdot 10^{-10}$   
electrostatic units.

*Avogadro's number* . . . . .  $N = (6.062 \pm 0.006) \cdot 10^{23}$   
per gram molecule.

*2/3 of the translation energy per degree*  $k = (1.372 \pm 0.002) \cdot 10^{-16}$   
erg per degree.

For  $h$  Millikan gives a value which he has derived by means of  $e$  and  $e/m$  from Rydberg's constant (known with great accuracy) and which agrees very well with the values derived by him from his experiments on the photo-electric effect and by Webster from wave-length measurements on induced  $X$ -rays. This value is

*Quantum of action* . . . . .  $h = (6.547 \pm 0.011) \cdot 10^{-27}$  erg sec.

We may add the value of the constant  $m$  appearing in Boltzmann's law (Art. 27). From the quoted values of  $h$  and  $k$  follows, in close agreement with Coblentz's measurements,

$$m = (7.63 \pm 0.045) \cdot 10^{-15} \text{ erg cm.}^{-3} \text{ degree}^{-1}.$$

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# THE THEORY OF QUANTA

(1916-1917)





## THE THEORY OF QUANTA

### 1. INTRODUCTION OF THE QUANTUM HYPOTHESIS

IN his treatment of the radiation phenomena Planck has assumed that the vibrators can take up and give out energy only in certain finite amounts, viz. multiples of the so-called energy element or quantum of energy. About this energy element he has at first made no special assumption. But later on, in view of Wien's law, it has appeared necessary to make it proportional to the frequency  $\nu$  of the vibrator. It could thus be written  $h\nu$ . Here

$$h = 6.415 \cdot 10^{-27} \text{ erg sec.}$$

The dimensions of  $h$  are those of the product *energy*  $\times$  *time* =  $ML^2T^{-1}$ . Planck's constant  $h$  is therefore called also the element or the quantum of action. The moment of momentum or the moment of an impulse has the same dimensions.

### 2. BOHR'S THEORY

In inventing models of atoms, various physicists, as Kelvin, J. J. Thomson, Rutherford, and Bohr, were guided by the concept that the chemical atom is built up of equal positive and negative charges. Of these models we will consider here that developed by Bohr.\*

As in Rutherford's model, Bohr imagines the atom as consisting of a positive nucleus and a number  $N$  of electrons revolving about it in a regular configuration. Since the atom as a whole is neutral, the charge  $E$  of the nucleus must be equal and opposite

\* *Phil. Mag.*, xxvi. pp. 1, 476, 858; 1913. "On the quantum theory of line-spectra," Part I., *Kgl. Danske Vidensk. Selsk. Skrifter, naturvidensk. og mathem. A*, 8 Roekke IV., 1, 1918.

to that of all the electrons taken together. Thus, if  $-e$  be the charge of an electron,  $E = Ne$ .

From the investigations on the scattering of  $\alpha$ -particles, due to Rutherford, Geiger, and others, it appeared that these particles, though themselves material, must be considered capable of penetrating into the innermost of atoms without breaking them up.

To harmonize his atom model with this result Rutherford was compelled to ascribe to the positive nucleus an extremely small volume. The same does Bohr.

He then turns to build up, with the aid of as few hypotheses as possible, laws for the structure of the electron orbits which would agree with the outcome of experiment. The result of these attempts is surprisingly good.

Like Bohr, we will first consider the model of the hydrogen atom. For this atom Bohr puts  $N=1$ , so that it consists of a positive nucleus with the charge  $E=e$ , about which revolves an electron with the charge  $-e$ .

Further, Bohr assumes that the electron can describe only such circular orbits as satisfy a certain condition. This condition clashes with the laws of classical mechanics and electrodynamics but is in line with Planck's considerations on quanta.

In fact, Bohr's fundamental condition is that *the moment of momentum of the electron shall be a multiple of  $h/2\pi$* . This leaves only a discrete manifold of possible circular orbits [*stationary orbits*], while the passage from one of them to another has to be imagined as taking place by a jump. So long as the electron continues to move on the same orbit, there is, against the classical electromagnetic theory, no radiation of energy, and thus no emission of light. This takes place only when the electron passes or, rather, jumps from one orbit to another, *and the energy of the light then emitted is  $h\nu$* , if  $\nu$  be the frequency of the light. This assumption enables us to calculate the frequency; for this purpose it is enough to divide the decrease of the energy of the atom in the said passage by the constant  $h$ .

Let  $r$  be the distance of the electron from the nucleus. Then the attraction exerted upon it by the nucleus is  $\frac{Ee}{r^2} = \frac{q}{r^2}$ , and the potential energy, supposed to vanish for  $r = \infty$ ,

$$U = -\frac{q}{r}.$$

If  $m$  be the mass of the electron, its velocity  $v$  in circular motion will be determined by

$$\frac{mv^2}{r} = \frac{q}{r^2},$$

which gives

$$v = \sqrt{\frac{q}{mr}}.$$

The kinetic energy can therefore be written

$$T = \frac{1}{2}mv^2 = \frac{1}{2}\frac{q}{r} = -\frac{1}{2}U,$$

and the total energy becomes

$$A = T + U = \frac{1}{2}U.$$

The momentum is

$$mv = \sqrt{\frac{mq}{r}},$$

and the moment of momentum,

$$\sqrt{mqr}.$$

Thus the condition imposed by Bohr upon the motion of the electron can be written

$$\sqrt{mqr} = p\frac{h}{2\pi},$$

where  $p$  is an integer (quantum condition).

This gives for the radius of the circular orbit

$$r = \frac{1}{mq} \frac{h^2}{4\pi^2} p^2,$$

and for the total energy,

$$A = -\frac{1}{2}\frac{q}{r} = -\frac{1}{p^2} \frac{2\pi^2mq^2}{h^2}.$$

The energy is the greater, the greater the number  $p$  and therefore  $r$ .

Let us consider two states of motion, I and II, and let  $p_I > p_{II}$ . In a passage from I to II the energy will decrease by  $A_I - A_{II}$ , so that the frequency of light which is then emitted will be determined by the formula

$$h\nu = A_I - A_{II}.$$

This gives

$$\nu = \frac{2\pi^2me^2E^2}{h^3} \left( \frac{1}{p_{II}^2} - \frac{1}{p_I^2} \right).$$

If the values (in usual electrostatic units)

$$e = 4.77 \cdot 10^{-10}, \quad E = 4.77 \cdot 10^{-10}, \quad \frac{e}{m} = 5.31 \cdot 10^{17}, \quad h = 6.415 \cdot 10^{-27}$$

be substituted,

$$\nu = 3.48 \cdot 10^{15} \left( \frac{1}{p_{II}^2} - \frac{1}{p_I^2} \right).$$

If one compares this formula for the case  $p_{II} = 2$  with Balmer's formula

$$\nu = 3.29 \cdot 10^{15} \left( \frac{1}{4} - \frac{1}{p^2} \right),$$

one must admit that the agreement is striking.

### 3. DEBYE'S THEORY OF THE ZEEMAN EFFECT

Debye has extended Bohr's theory, and proposed so to modify the model of the atom, or rather Bohr's quantum condition, as to be able to account for the splitting of the spectrum lines in a magnetic field.

Like Bohr, he considers an electron  $-e$  which moves about a positive nucleus  $+E$ , but instead of the particular case of circular orbits he treats the more general one in which the electron describes ellipses. If the position of the electron is referred to a fixed co-ordinate system  $X, Y, Z$  whose origin is occupied by the positive nucleus, and if the positive  $Z$ -axis is taken along the lines of the magnetic field  $H$ , then the equations of motion of the electron are

$$m\ddot{x} = -q \frac{x}{r^3} - \frac{eH}{c} \dot{y},$$

$$m\ddot{y} = -q \frac{y}{r^3} + \frac{eH}{c} \dot{x},$$

$$m\ddot{z} = -q \frac{z}{r^3}.$$

If  $H=0$ , these equations are obviously satisfied by elliptic motion. What form of motion does satisfy them in the case of  $H \neq 0$ ?

These equations can only be integrated for not too strong field intensities. For this purpose we introduce a new system of co-ordinates having with the old one the  $Z$ -axis in common and

rotating about this axis with the constant angular velocity  $\omega$ . Thus the new co-ordinates are

$$\begin{aligned}x' &= x \cos \omega t + y \sin \omega t, \\y' &= -x \sin \omega t + y \cos \omega t, \\z' &= z.\end{aligned}$$

We will assume that  $\omega$  is so small that terms containing  $\omega^2$  can be neglected. This amounts to omitting the centrifugal force and, with regard to the Zeeman effect, to considering a splitting in which the change of wave-length is small compared with the wave-length itself. If the equations of motion are written in the new co-ordinates, it appears that the terms containing the velocities drop out provided that we make  $\omega = \frac{eH}{2mc}$ .

The equations of motion then become

$$\begin{aligned}m\ddot{x}' &= -q\frac{x'}{r^3}, \\m\ddot{y}' &= -q\frac{y'}{r^3}, \\m\ddot{z}' &= -q\frac{z'}{r^3}.\end{aligned}$$

These have the same form as the equations in  $x, y, z$  for the case  $H=0$ . Thus, if  $H$  differs from zero, the equations will still be satisfied by motions in elliptic orbits, but these ellipses, which are at rest in the moving system  $X', Y', Z'$ , will in the fixed co-ordinate system rotate about the  $Z$ -axis (direction of the field) with an angular velocity  $\omega$  proportional to the field intensity. Since our electrons are negative, so that  $e$  is positive, this rotation will take place in the sense corresponding to the field direction. Thus, to find the motion of the electrons in the magnetic field  $H$ , we have only to give to the electronic orbits which would be described in the absence of a magnetic field a rotatory motion about the direction of  $H$ . ✱

In order to get the splitting of the spectrum lines we require more than one quantum condition. Now, Debye characterizes the state by the energy  $A$  and the moment of momentum  $M$  corresponding to the motion relatively to the *spinning* axes, and he requires (cf. the second formula for  $A$  on p. 281) that

$$q\sqrt{\frac{m}{-2A}} = p_1 \frac{h}{2\pi}$$

and

$$M = p_2 \frac{h}{2\pi},$$

where  $p_1, p_2$  are integers. If there is a magnetic field, he adds the condition

$$M_0 = p_3 \frac{h}{2\pi},$$

where  $M_0$  is the projection of the moment of momentum upon the plane  $V$  perpendicular to  $H$ . Finally, as in Bohr's case without the magnetic field, the frequency of radiation in the presence of a magnetic field is still to be given by the energy loss of the atom divided by  $h$ .

As has just been said,  $A$  is the energy with respect to the spinning axes. In order to find herefrom the energy relative to the fixed axes (as required for the application of the rule just mentioned), we lay through the electron  $P$  a plane  $V$  perpendicular to the  $Z$ -axis. Let  $O$  be the intersection point of  $V$  with the  $Z$ -axis. Let us resolve the velocity of the electron relative to the system  $X', Y', Z'$  into a component  $v_1$  parallel to  $OZ$ , a component  $v_2$  in the direction  $OP$ , and a component  $v_3$  in  $V$  perpendicular to  $OP$ . It is clear that  $M_0 = mv_3 \cdot OP$ .

In passing from the spinning to the fixed axes  $X, Y, Z$  the velocity component  $v_3$  only will be changed, viz. by the amount  $\omega \cdot OP$ .

The energy will increase by

$$m\omega v_3 \cdot OP = p_3 \omega \frac{h}{2\pi},$$

and thus from  $-2\pi^2 q^2 m / p_1^2 h^2$  will change to

$$-\frac{2\pi^2 q^2 m}{p_1^2 h^2} + p_3 \omega \frac{h}{2\pi}.$$

If now the electron passes from  $p_1, p_3$  to  $p'_1, p'_3$  ( $p_1 > p'_1$ ), so that radiation takes place, the frequency of the emitted light will be determined by the equation

$$h\nu = \frac{2\pi^2 q^2 m}{h^2} \left( \frac{1}{p'^1_1{}^2} - \frac{1}{p_1^2} \right) + (p_3 - p'_3) \omega \frac{h}{2\pi},$$

which gives

$$\nu = \frac{2\pi^2 q^2 m}{h^3} \left( \frac{1}{p'^1_1{}^2} - \frac{1}{p_1^2} \right) + (p_3 - p'_3) \frac{\omega}{2\pi}.$$



Manifestly the second term expresses a magnetic splitting. For a fixed value of  $p'_1$  and different values of  $p_1$  we have a [Balmer-like] series of which all the lines show the same Zeeman effect.

$$\text{For} \quad p_3 - p'_3 = \pm 1, \quad \Delta\nu = \pm \frac{\omega}{2\pi}.$$

This so-called normal splitting is thus proportional to the field intensity.

The values  $p_3 - p'_3 = 2, 3$ , etc., do not seem to occur.

Debye's results, as far as the hydrogen lines are concerned, are in satisfactory agreement with experiment. For this gives, indeed, in strong fields a normal triplet in the direction perpendicular to the field and a normal doublet in the longitudinal direction. In weak fields, however, the phenomena are more complicated.

4. Debye's theory can easily be extended to an atomic system of any structure in which, however, negative electrons only are moving. The equations of motion of one of them in the magnetic field  $H$  are

$$m\ddot{x}_1 + \frac{eH}{c} \dot{y}_1 = -\frac{\partial U}{\partial x_1},$$

$$m\ddot{y}_1 - \frac{eH}{c} \dot{x}_1 = -\frac{\partial U}{\partial y_1},$$

$$m\ddot{z}_1 = -\frac{\partial U}{\partial z_1}.$$

Let us introduce rotating axes through the equations

$$x'_1 = x_1 \cos \omega t + y_1 \sin \omega t,$$

$$y'_1 = -x_1 \sin \omega t + y_1 \cos \omega t; \quad z'_1 = z_1.$$

Then

$$\dot{x}'_1 = \dot{x}_1 \cos \omega t + \dot{y}_1 \sin \omega t - \omega x_1 \sin \omega t + \omega y_1 \cos \omega t$$

$$\dot{y}'_1 = -\dot{x}_1 \sin \omega t + \dot{y}_1 \cos \omega t - \omega x_1 \cos \omega t - \omega y_1 \sin \omega t$$

$$\ddot{x}'_1 = \ddot{x}_1 \cos \omega t + \ddot{y}_1 \sin \omega t - 2\omega \dot{x}_1 \sin \omega t + 2\omega \dot{y}_1 \cos \omega t$$

$$\ddot{y}'_1 = -\ddot{x}_1 \sin \omega t + \ddot{y}_1 \cos \omega t - 2\omega \dot{x}_1 \cos \omega t - 2\omega \dot{y}_1 \sin \omega t.$$

If we multiply the first of the equations of motion by  $\cos \omega t$ , the second by  $\sin \omega t$  and add them, then the left-hand member

reduces to  $m\ddot{x}'_1$ , provided we put  $\omega = \frac{eH}{2cm}$ , as before. The right-hand member becomes  $-\partial U/\partial x'_1$ , so that

$$m\ddot{x}'_1 = -\frac{\partial U}{\partial x'_1},$$

and similarly,

$$m\ddot{y}'_1 = -\frac{\partial U}{\partial y'_1},$$

$$m\ddot{z}'_1 = -\frac{\partial U}{\partial z'_1},$$

with equations of the same form for the remaining electrons.

The effect of a magnetic field is thus seen to amount to a rotation of the moving system with the angular velocity  $\omega$ .

Suppose, first, there is no magnetic field, and let it be possible to specify some states of motion by means of Planck's constant  $h$  and the integers  $p_1, p_2$ . Let the energy of the system be expressed by a function of these integers. Then, passing from  $p_1, p_2$  to  $p'_1, p'_2$ , we shall have

$$\nu = \frac{1}{h}\{F(p_1, p_2) - F(p'_1, p'_2)\},$$

which will give us spectrum series.

Let now, in the presence of a magnetic field, the rule of specifying the motions by means of the numbers  $p_1, p_2$  remain as before, but with the supplementary condition

$$M_0 = p_3 \frac{h}{2\pi},$$

where  $M_0$  is the aforesaid component of the moment of momentum. Then the energy will become

$$F(p_1, p_2) + p_3 \omega \frac{h}{2\pi},$$

and the frequency,

$$\nu = \frac{1}{h}\{F(p_1, p_2) - F(p'_1, p'_2)\} + (p_3 - p'_3) \frac{\omega}{2\pi}.$$

Thus we find always the same type of the Zeeman effect. The other types remain, thus far, unexplained. ✕

## 5. EPSTEIN'S THEORY OF THE STARK EFFECT. INTRODUCTION

Epstein avails himself of a method based upon the principle of least action and the associated partial differential equation, on which Jacobi has made the solution of mechanical problems depend. It may be well to recall here some general theorems related to this subject. In doing so we will limit ourselves to the motion of a particle in a field of force. Let the particle placed in this field have the potential energy  $U$ , and let  $T$  be its kinetic energy.

For any conceivable motion, in which the particle describes some orbit or other, we can consider the integral

$$H = \int_{t_0}^t (T - U) dt.$$

In this expression there is manifestly no trace of co-ordinates. Whether we use rectangular co-ordinates  $x, y, z$  or any other co-ordinates  $q_1, q_2, q_3$ , will have no influence upon  $T - U$  and  $H$ . For the sake of generality let us first work with  $q_1, q_2, q_3$ .  $U$  will be a function of these co-ordinates and  $T$  a homogeneous quadratic function of  $\dot{q}_1, \dot{q}_2, \dot{q}_3$  with coefficients which may depend on the co-ordinates. The components of momentum will be

$$\frac{\partial T}{\partial \dot{q}_1} = p_1, \quad \frac{\partial T}{\partial \dot{q}_2} = p_2, \quad \frac{\partial T}{\partial \dot{q}_3} = p_3.$$

Let us now change  $t, q_1, q_2, q_3$  by  $\delta t, \delta q_1, \delta q_2, \delta q_3$  and consider the motion thus varied, in which, that is, the co-ordinates have at the instant  $t + \delta t$  the values  $q_1 + \delta q_1, q_2 + \delta q_2, q_3 + \delta q_3$ , the four variations  $\delta t, \delta q_1, \delta q_2, \delta q_3$  being all functions of  $t$ . What is the corresponding change of the integral? The symbol  $\delta$  denotes, in general, the difference between corresponding magnitudes in the original and the varied motion, while  $d$  indicates the difference of the values of a magnitude at the instants  $t$  and  $t + dt$ .

We have

$$\delta \delta t = \delta dt, \quad d\delta q_1 = \delta dq_1, \text{ etc.}$$

The varied value of a velocity is

$$\frac{dq + \delta dq}{dt + \delta dt} = \dot{q} + \frac{d\delta q}{dt} - \dot{q} \frac{d\delta t}{dt},$$

whence

$$\delta \dot{q} = \frac{d\delta q}{dt} - \dot{q} \frac{d\delta t}{dt}.$$

and therefore,

$$\begin{aligned}\delta T &= \sum \frac{\partial T}{\partial q} \delta q + \sum \frac{\partial T}{\partial \dot{q}} \delta \dot{q} \\ &= \sum \frac{\partial T}{\partial q} \delta q + \sum \frac{\partial T}{\partial \dot{q}} \frac{d\delta q}{dt} - \frac{d\delta t}{dt} \sum \dot{q} \frac{\partial T}{\partial \dot{q}} \\ &= \frac{d}{dt} \sum p \delta q + \sum \left( \frac{\partial T}{\partial q} - \frac{d}{dt} \frac{\partial T}{\partial \dot{q}} \right) \delta q - 2T \frac{d\delta t}{dt}.\end{aligned}$$

Now, since

$$\delta \{ (T - U) dt \} = (\delta T - \delta U) dt + (T - U) d\delta t,$$

we have

$$\delta H = \int_{t_0}^t \sum \left\{ \frac{\partial (T - U)}{\partial q} - \frac{d}{dt} \frac{\partial T}{\partial \dot{q}} \right\} \delta q dt + \int_{t_0}^t A d\delta t + \left| \sum p \delta q \right|_{t_0}^t, \quad (1)$$

where  $A = -(T + U)$ .

This equation holds generally. The original motion may be any conceivable motion; nor has anything been assumed about the variations.

If we now require that for a *natural* motion, i.e. one which can actually take place in the given field of force,

$$\delta H = 0,$$

provided the initial and the final state as well as the terminal values of the time are not varied (Hamilton's principle), then we get Lagrange's equations of motion,

$$\frac{\partial (T - U)}{\partial q} - \frac{d}{dt} \frac{\partial T}{\partial \dot{q}} = 0.$$

Thus, if the original motion is a natural motion, the general equation reduces to

$$\delta H = A \delta(t - t_0) + \left| \sum p \delta q \right|_{t_0}^t,$$

where the property has been used that in a natural motion  $A = -(T + U)$ , the negated energy, is a constant.

The last formula for  $\delta H$  can also be applied to a variation of the original natural motion which leaves it natural. The initial state being chosen, a natural motion can be completely determined by its end state ( $q_1, q_2, q_3$ ) and the time  $t - t_0$  required to reach it.  $H$  is then a function of these data and we have

$$\delta H = p_1 \delta q_1 + p_2 \delta q_2 + p_3 \delta q_3 + A \delta(t - t_0).$$

From what has been said we can derive some properties of the function

$$W = H - A(t - t_0), \quad . \quad . \quad . \quad . \quad (2)$$

which, as well as  $H$ , has obviously for every natural motion a determined value. If we so vary the natural motion that it always remains natural, then, by the last two equations,

$$\delta W = p_1 \delta q_1 + p_2 \delta q_2 + p_3 \delta q_3 - (t - t_0) \delta A.$$

Whence we see that, if we propose to work with the function  $W$ , it is convenient to determine the motion, in addition to the initial state, by the final state and the energy  $-A$ . Then  $W$  will be a function of these data and we shall have

$$\frac{\partial W}{\partial q_1} = p_1, \quad \frac{\partial W}{\partial q_2} = p_2, \quad \frac{\partial W}{\partial q_3} = p_3, \quad . \quad . \quad . \quad (3)$$

$$\frac{\partial W}{\partial A} = -(t - t_0). \quad . \quad . \quad . \quad . \quad (4)$$

The function  $W$  has an important property. In fact, our equation (1) holds for every variation of any conceivable motion. Now, suppose that the original motion is a natural motion, so that throughout it

$$A = -(T + U)$$

remains constant; leave the initial and the final state unaltered, and having chosen the varied path adjust the velocity with which it is described so that in the varied motion  $T + U$  shall have the same value  $-A$  as in the original motion. Then, by (2),

$$\delta W = \delta H - A \delta(t - t_0),$$

and since

$$\delta H = A \delta(t - t_0),$$

$$\delta W = 0.$$

This is *the principle of least action*. For since, by what has just been assumed, in the disturbed as well as in the original motion  $A = -(T + U)$  has a constant value, we can replace  $A(t - t_0)$  by  $-\int_{t_0}^t (T + U) dt$  and therefore, in view of the definition of  $H$ , the function  $W$  by

$$\int_{t_0}^t 2T dt, \quad . \quad . \quad . \quad . \quad (5)$$

and it is this integral which is called "action".

We can write it also

$$m \int_{P_0}^P v ds = \int_{P_0}^P \sqrt{-2m(A+U)} ds, \quad . \quad . \quad . \quad (6)$$

where  $ds$  is an element of the path, the integral being extended from the initial state  $P_0$  to the final state  $P$ .

It may be well to mention that the function defined by (2) coincides with the action (5) for every natural motion and also for those disturbed motions implied in the principle of least action, but that for other disturbed motions (2) and (5) may differ from each other.

Let us now consider natural motions to which corresponds a fixed value  $-A$  of the energy. Then, the initial state being kept fixed,  $W$  is a function of the end co-ordinates. If we introduce rectangular co-ordinates  $x, y, z$ , then

$$\frac{\partial W}{\partial x} = m\dot{x}, \quad \frac{\partial W}{\partial y} = m\dot{y}, \quad \frac{\partial W}{\partial z} = m\dot{z}, \quad . \quad . \quad . \quad (7)$$

and since  $T + U = -A$ ,

$$\dot{x}^2 + \dot{y}^2 + \dot{z}^2 = -\frac{2}{m}(U + A), \quad . \quad . \quad . \quad (8)$$

which can be written

$$\left(\frac{\partial W}{\partial x}\right)^2 + \left(\frac{\partial W}{\partial y}\right)^2 + \left(\frac{\partial W}{\partial z}\right)^2 = -2m(U + A). \quad . \quad . \quad (9)$$

This equation, which says that the gradient of the function  $W$  has at each point of space a prescribed value, is *Jacobi's differential equation*. It has here been derived under the assumption that  $W$  is the action reckoned from a fixed initial point  $P_0$ . But the equation is satisfied also by other functions, having another, though similar, physical significance.

Suppose that  $W(x, y, z)$  is some function satisfying the differential equation (9) and consider the surfaces  $W = \text{const.}$  It can, first of all, be proved that their orthogonal trajectories are possible paths.

Consider two successive surfaces  $W = C$  and  $W = C + dC$  and imagine a line-element  $ds$  drawn between them, normal to  $W = C$ , so that  $dW/ds$  is the gradient. Then, by (9),

$$\frac{dW}{ds} = \sqrt{-2m(U + A)},$$



and, since  $dW = dC$ ,

$$\sqrt{-2m(U+A)}ds = dC.$$

If, however,  $ds'$  is an oblique element between the two surfaces, making an angle  $\theta$  with the normal, then

$$\sqrt{-2m(H+A)}ds' = \sqrt{-2m(U+A)} \frac{ds}{\cos \theta} = \frac{1}{\cos \theta} dC.$$

It follows that for a segment of an orthogonal trajectory contained between two points  $P_0$  and  $P$ , compared with neighbouring lines,

$$\delta \int \sqrt{-2m(U+A)}ds = 0,$$

and since, by the principle of least action, this equation characterizes a natural path, we have thus proved that the orthogonal trajectories of the surfaces  $W = \text{const.}$  are such paths.

Having found this, we can easily see the meaning of  $W$ . In fact, if we pass from the surface  $W = C$  to  $W = C + dC$ , we have, for the intercepted element of the orthogonal trajectory,

$$\sqrt{-2m(U+A)}ds = dC = dW,$$

so that  $W$  represents at any point of such a trajectory the integral

$$\int \sqrt{-2m(U+A)}ds,$$

reckoned from the surface  $W = 0$ . Thus, an arbitrary solution of the differential equation represents the action  $W$ , reckoned not from a fixed point, but from a certain surface, along a path perpendicular to it. This shows the great variety of possible solutions. For the surface  $W = 0$  can be chosen arbitrarily.

In what follows the action taken from a point  $P_0$  up to a point  $P$  will be denoted by  $W_{P_0}^P$ .

Suppose that we have a solution of the differential equation which contains an undetermined non-additive constant  $c$ ,  $W = F(x, y, z, c)$ . Consider the corresponding surfaces  $W = \text{const.}$  and the paths which are their orthogonal trajectories. Then along each of these paths  $\partial W / \partial c$  will be constant. (Notice that  $c$  is not an additive constant; otherwise the theorem would be trivial.)

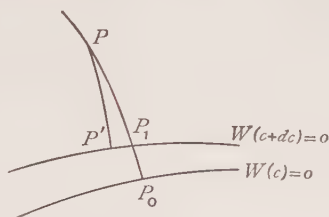


FIG. 1.

*Proof.* Consider the surfaces  $W(c)=0$  and  $W(c+dc)=0$ . Let  $P_0$  be a point of the former,  $P_0P$  a path starting normally from it, and  $P$  an arbitrary point on this path. Let this path cut the surface  $W(c+dc)=0$  at  $P_1$ . Further, let  $P'P$  be the path through  $P$  which starts perpendicularly to the latter surface from a point  $P'$ . The points  $P_0$  and  $P_1$  are infinitely near each other. Now, we have at the point  $P$

$$W(c)=W_{P_0}P, \quad W(c+dc)=W_{P'}P=W_{P_1}P,*$$

and therefore,

$$\frac{\partial W}{\partial c} = - \frac{W_{P_0}P_1}{dc},$$

which has the same value for all points of the path  $P_0P$ . Q.E.D.

From this theorem the following one can be derived: If we have a solution of the differential equation with two non-additive constants  $c_1$  and  $c_2$ , then

$$\frac{\partial W}{\partial c_1} = \gamma_1, \quad \frac{\partial W}{\partial c_2} = \gamma_2$$

with two new constants  $\gamma_1, \gamma_2$  are the equations of a path.

Since we have assigned to  $A$  a fixed value, a solution  $W$  of Jacobi's differential equation will contain also the constant  $A$  and we can consider the derivative  $\partial W/\partial A$ . This gives rise to a

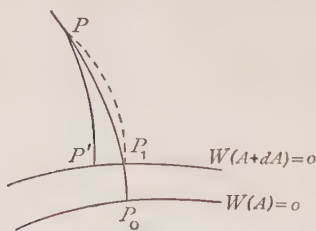


FIG. 2.

reasoning similar to the preceding one with the difference, however, that now we have to consider, for given terminal points, two different actions, viz. those corresponding to the values  $A$  and  $A + dA$ . The corresponding figure (Fig. 2) is as before, but it contains in addition a dotted line between  $P_1$  and  $P$ . This

represents the path between these points which is described with the energy  $-(A + dA)$ , while the continuous line  $P_0 P_1 P$  represents the path for the value  $-A$  of the energy. The energy belonging to the path  $P'P$  is  $-(A + dA)$ .

\* We see from the equations (7) that  $W$  does not change if the path is varied by displacing the end-point over an infinitesimal distance perpendicularly to the path itself; hence  $W_{P'}P = W_{P_1}P$ .

Now, at the point  $P$ ,

$$W(A) = W_{P_0}{}^P(A) = W_{P_0}{}^{P_1}(A) + W_{P_1}{}^P(A),$$

$$W(A + dA) = W_{P_0}{}^P(A + dA) = W_{P_1}{}^P(A + dA),$$

so that 
$$\frac{\partial W}{\partial A} = -\frac{W_{P_0}{}^{P_1}(A)}{dA} + \frac{\partial}{\partial A} W_{P_1}{}^P.$$

The first term has a value  $C$  which will be the same independently of the choice of the point  $P$  on the line  $P_0P$ . The second term is, by (4), equal to  $-(t - t_1)$ , if  $P$  be reached at the instant  $t$  and  $P_1$  at  $t_1$ . Thus, introducing the constant  $t_1 + C = t_0$ , we have the equation

$$\frac{\partial W}{\partial A} = -(t - t_0), \quad . \quad . \quad . \quad . \quad (10)$$

which tells us how the path is described in time.

*Remarks:* (1) If we agree to consider only such motions for which  $A$  has a given value, the velocity at each point of space is fixed. Now, with these fixed velocities an arbitrary line could be described, but the actual paths are those determined by the condition  $\delta \int v ds = 0$ . Cf. (6).

(2) These relations can be illustrated by considering the motion of light in a non-homogeneous but isotropic medium from the standpoint of the emission theory. The velocity is then also a given function of the co-ordinates, and the actual course of a light ray is determined by the condition  $\delta \int v ds = 0$ .

(3) Also when treated on the wave theory does the last problem harmonize with our dynamical considerations. If the propagation velocity of light as function of the co-ordinates is given by  $1/\sqrt{-2m(A+U)}$ , which is always conceivable, then  $W$  represents the time which light requires to cover a certain path. The surfaces  $W = \text{const.}$  give the successive positions of a wave-front which can be derived from each other by Huygens' construction and whose orthogonal trajectories are the light rays.

(4) In deriving the partial differential equation for  $W$  we have introduced as independent variables the rectangular co-ordinates  $x, y, z$ , but we might as well have taken other co-ordinates  $q_1, q_2, q_3$ . In fact, (8) can be written

$$\frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = -(U + A),$$

and we need only express the kinetic energy appearing in the right-hand member as a quadratic function of the momenta

$p_1, p_2, p_3$  corresponding to the co-ordinates  $q_1, q_2, q_3$  and then replace  $p_1, p_2, p_3$  by  $\frac{\partial W}{\partial q_1}, \frac{\partial W}{\partial q_2}, \frac{\partial W}{\partial q_3}$ .

Of course, the partial differential equation thus obtained is no new relation; it is still the equation (9), only written in new independent variables.

Again, what has been said about the properties of the solutions of this differential equation is independent of the choice of the co-ordinates. If we have a solution  $W$  which besides any such co-ordinates and the energy  $-A$  contains two non-additive constants, we shall still obtain the path equations by equating the derivatives of  $W$  with respect to those constants to two new constants. Also equation (10) remains valid.

We will now apply the method just explained to the problem of an atom placed in an electric field.

## 6. EPSTEIN'S TREATMENT OF THE PROBLEM

Epstein proposes to set up the quantum conditions for the motion of the electron in an atom placed in a constant electric field in such a way as to be able to account for the splitting of the spectrum lines as found by Stark.

As has already been mentioned, he starts from Jacobi's differential equation. Epstein's first task is thus to express  $W$  in properly chosen co-ordinates. These he determines as follows:

The origin being placed in the nucleus, the axis  $OX$  is drawn in the direction of the external force  $E$ . In the plane laid through the electron and  $OX$  an axis  $OY$  perpendicular to  $OX$  is drawn;  $x$  and  $y$  are the co-ordinates of the electron in the rotating  $xy$ -plane, and  $\phi$  is the angle which this plane makes with one of its own positions. Thus the rectangular co-ordinates of the electron are

$$x, y \cos \phi, y \sin \phi,$$

and its velocity components,

$$\dot{x}, \dot{y} \cos \phi - y\dot{\phi} \sin \phi, \dot{y} \sin \phi + y\dot{\phi} \cos \phi.$$

The kinetic energy is

$$T = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + y^2\dot{\phi}^2),$$

and the potential energy,

$$U = -\frac{\kappa e^2}{r} + eEx,$$

where  $\kappa e$  is the charge of the nucleus and  $-e$  that of the electron. Next, Epstein replaces the co-ordinates  $x, y$  by  $\xi$  and  $\eta$  which are defined by the transformation formula

$$x + iy = \frac{1}{2}(\xi + i\eta)^2 = \frac{1}{2}(\xi^2 - \eta^2) + i\xi\eta.$$

This gives

$$\begin{aligned} x &= \frac{1}{2}(\xi^2 - \eta^2), & y &= \xi\eta, & r &= \sqrt{x^2 + y^2} = \frac{1}{2}(\xi^2 + \eta^2); \\ \dot{x} &= \xi\dot{\xi} - \eta\dot{\eta}, & \dot{y} &= \xi\dot{\eta} + \eta\dot{\xi}, & \dot{x}^2 + \dot{y}^2 &= (\dot{\xi}^2 + \dot{\eta}^2)(\xi^2 + \eta^2), \\ T &= \frac{1}{2}m(\dot{\xi}^2 + \dot{\eta}^2)(\xi^2 + \eta^2) + \frac{1}{2}m\xi^2\eta^2\dot{\phi}^2, \\ p_\xi &= m(\dot{\xi}^2 + \eta^2)\dot{\xi}, & p_\eta &= m(\xi^2 + \dot{\eta}^2)\dot{\eta}, & p_\phi &= m\xi^2\eta^2\dot{\phi}, \\ T &= \frac{1}{2}\frac{p_\xi^2 + p_\eta^2}{m(\xi^2 + \eta^2)} + \frac{1}{2m}\frac{p_\phi^2}{\xi^2\eta^2}, \\ U &= -\frac{2\kappa e^2}{\xi^2 + \eta^2} + \frac{eE}{2}(\xi^2 - \eta^2). \end{aligned}$$

Thus the differential equation (9) for  $W$  assumes the form

$$\begin{aligned} \frac{1}{2m(\xi^2 + \eta^2)} \left\{ \left( \frac{\partial W}{\partial \xi} \right)^2 + \left( \frac{\partial W}{\partial \eta} \right)^2 \right\} + \frac{1}{2m\xi^2\eta^2} \left( \frac{\partial W}{\partial \phi} \right)^2 \\ - \frac{2\kappa e^2}{\xi^2 + \eta^2} + \frac{eE}{2}(\xi^2 - \eta^2) + A = 0 \\ \text{or} \\ \left( \frac{\partial W}{\partial \xi} \right)^2 + \left( \frac{\partial W}{\partial \eta} \right)^2 + \left( \frac{1}{\xi^2} + \frac{1}{\eta^2} \right) \left( \frac{\partial W}{\partial \phi} \right)^2 \\ - 4\kappa me^2 + meE(\xi^4 - \eta^4) + 2mA(\xi^2 + \eta^2) = 0. \quad (11) \end{aligned}$$

Now, this equation can be satisfied by a sum of three terms each of which contains only one of the co-ordinates  $\phi, \xi, \eta$ . For the first of these we can take  $\phi$  itself multiplied by a constant, say  $\sqrt{ma}\phi$ , and for the other terms we will write  $W_1(\xi)$  and  $W_2(\eta)$ , so that

$$W = \sqrt{ma}\phi + W_1(\xi) + W_2(\eta).$$

We see at once that (11) will be satisfied if we put

$$\begin{aligned} \left( \frac{dW_1}{d\xi} \right)^2 + \frac{ma^2}{\xi^2} - 2me^2(\kappa + \beta) + meE\xi^4 + 2mA\xi^2 &= 0, \\ \left( \frac{dW_2}{d\eta} \right)^2 + \frac{ma^2}{\eta^2} - 2me^2(\kappa - \beta) - meE\eta^4 + 2MA\eta^2 &= 0, \end{aligned}$$

where  $\beta$  is a new constant.

These equations can be written

$$\frac{dW_1}{d\xi} = \sqrt{mf_1(\xi)}, \quad \frac{dW_2}{d\eta} = \sqrt{mf_2(\eta)}, \quad (12)$$

where

$$f_1(\xi) = -\frac{\alpha^2}{\xi^2} - eE\xi^4 - 2A\xi^2 + 2e^2(\kappa + \beta),$$

$$f_2(\eta) = -\frac{\alpha^2}{\eta^2} + eE\eta^4 - 2A\eta^2 + 2e^2(\kappa - \beta).$$

Thus we have the solution

$$W = \sqrt{m}[\alpha\phi + \int \sqrt{f_1(\xi)} d\xi + \int \sqrt{f_2(\eta)} d\eta], \quad (13)$$

which apart from  $A$  (and a pair of additive, and therefore irrelevant, constants) contains the constants  $\alpha$  and  $\beta$ .

Let us first note that the value of the momentum  $p_\phi$  is

$$p_\phi = \frac{\partial W}{\partial \phi} = \sqrt{m}\alpha,$$

and those of the remaining two momenta, by (3) and (12),

$$p_\xi = \sqrt{mf_1(\xi)} \quad \text{and} \quad p_\eta = \sqrt{mf_2(\eta)}.$$

Next, equating the derivatives of (13) with respect to  $\beta$ ,  $\alpha$ , and  $A$  to  $e^2\sqrt{m}\beta'$ ,  $\sqrt{m}\phi_0$ , and  $-(t-t_0)$  respectively, where  $\beta'$ ,  $\phi_0$ ,  $t_0$  are constants, we have

$$\begin{aligned} \int \frac{d\xi}{\sqrt{f_1(\xi)}} - \int \frac{d\eta}{\sqrt{f_2(\eta)}} &= \beta', \\ \int \frac{d\xi}{\xi^2 \sqrt{f_1(\xi)}} + \int \frac{d\eta}{\eta^2 \sqrt{f_2(\eta)}} &= \frac{\phi - \phi_0}{\alpha}, \\ \int \frac{\xi^2 d\xi}{\sqrt{f_1(\xi)}} + \int \frac{\eta^2 d\eta}{\sqrt{f_2(\eta)}} &= \frac{1}{\sqrt{m}}(t - t_0), \end{aligned}$$

three equations determining the motion of the electron.

The main point in this method is that the differential equation can be satisfied by a sum of three functions, each of which depends only on one co-ordinate.

The last three equations will be derived in the next article in another way.

## 7. ANOTHER DERIVATION OF EPSTEIN'S FORMULAE.

### THEORY OF STARK EFFECT CONTINUED.

We consider again the possible motions in an electric field.

The electron  $-e$  moves again around a fixed positive charge



+  $\kappa e$  under the influence of a constant electric force  $E$  directed along the  $X$ -axis. The potential energy is

$$U = -\frac{\kappa e^2}{r} + eEx$$

or in Epstein's co-ordinates  $\xi, \eta$ , as in Art 6,

$$U = -\frac{2\kappa e^2}{\xi^2 + \eta^2} + \frac{1}{2}eE(\xi^2 - \eta^2),$$

and the kinetic energy, as found in the same article,

$$T = \frac{1}{2}m(\dot{\xi}^2 + \dot{\eta}^2)(\xi^2 + \eta^2) + \frac{1}{2}m\xi^2\eta^2\dot{\phi}^2.$$

We will now work with Lagrange's equations. One of these, that corresponding to  $\phi$ , gives

$$\frac{\partial T}{\partial \dot{\phi}} = \sqrt{m}a,$$

where  $a$  is a constant, or, by the last expression for  $T$ ,

$$\dot{\phi} = \frac{a}{\sqrt{m}} \frac{1}{\xi^2 \eta^2}. \quad (14)$$

The remaining two Lagrangian equations, corresponding to  $\xi, \eta$ , are

$$\frac{d}{dt} \left( \frac{\partial T}{\partial \dot{\xi}} \right) - \frac{\partial T}{\partial \xi} = -\frac{\partial U}{\partial \xi},$$

$$\frac{d}{dt} \left( \frac{\partial T}{\partial \dot{\eta}} \right) - \frac{\partial T}{\partial \eta} = -\frac{\partial U}{\partial \eta},$$

or, with the above expressions for  $T, U$  and after the substitution of the value (14) for  $\dot{\phi}$ ,

$$\frac{d}{dt} \{ m(\xi^2 + \eta^2) \dot{\xi} \} = m\xi(\dot{\xi}^2 + \dot{\eta}^2) + \frac{a^2}{\xi^3 \eta^2} - \frac{4\kappa e^2 \xi}{(\xi^2 + \eta^2)^2} - eE\xi, \quad (15)$$

$$\frac{d}{dt} \{ m(\xi^2 + \eta^2) \dot{\eta} \} = m\eta(\dot{\xi}^2 + \dot{\eta}^2) + \frac{a^2}{\xi^2 \eta^3} - \frac{4\kappa e^2 \eta}{(\xi^2 + \eta^2)^2} + eE\eta. \quad (16)$$

These equations can be simplified by making use of the energy equation. The latter is

$$T + U = -A$$

or, again by (14),

$$\frac{1}{2}m(\xi^2 + \eta^2)(\dot{\xi}^2 + \dot{\eta}^2) + \frac{a^2}{2\xi^2\eta^2} - \frac{2\kappa e^2}{\xi^2 + \eta^2} + \frac{1}{2}eE(\xi^2 - \eta^2) = -A. \quad (17)$$

Substitute the value of  $(\dot{\xi}^2 + \dot{\eta}^2)$  following from this equation

into (15) and (16) and multiply by  $(\xi^2 + \eta^2)$ . The terms with  $e^2$  will disappear and the result will be

$$(\xi^2 + \eta^2) \frac{d}{dt} \{m(\xi^2 + \eta^2)\dot{\xi}\} = \frac{\alpha^2}{\xi^3} - 2eE\xi^3 - 2A\xi, \quad . \quad (18)$$

$$(\xi^2 + \eta^2) \frac{d}{dt} \{m(\xi^2 + \eta^2)\dot{\eta}\} = \frac{\alpha^2}{\eta^3} + 2eE\eta^3 - 2A\eta. \quad . \quad (19)$$

The remarkable feature of these equations is that the right-hand member of (18) contains only  $\xi$  and that of (19) only  $\eta$ . Owing to this circumstance and to the form of the left-hand members these equations can be integrated. In fact, multiplying (18) by  $\dot{\xi}$  and (19) by  $\dot{\eta}$ , we find at once

$$\frac{1}{2}m(\xi^2 + \eta^2)^2\dot{\xi}^2 = -\frac{1}{2}\frac{\alpha^2}{\xi^2} - \frac{1}{2}eE\xi^4 - A\xi^2 + C_1, \quad . \quad (20)$$

$$\frac{1}{2}m(\xi^2 + \eta^2)^2\dot{\eta}^2 = -\frac{1}{2}\frac{\alpha^2}{\eta^2} + \frac{1}{2}eE\eta^4 - A\eta^2 + C_2, \quad . \quad (21)$$

where  $C_1$  and  $C_2$  are integration constants.

In view of the energy equation these two constants can be reduced to a single one; instead of  $C_1$  and  $C_2$  we can introduce the previous constant (energy)  $-A$  and but one more constant  $\beta$ . In fact, adding (20) and (21) and dividing by  $(\xi^2 + \eta^2)$ , we have

$$\frac{1}{2}m(\xi^2 + \eta^2)(\dot{\xi}^2 + \dot{\eta}^2) = -\frac{\alpha^2}{2\xi^2\eta^2} + \frac{1}{2}eE(\eta^2 - \xi^2) - A + \frac{C_1 + C_2}{\xi^2 + \eta^2},$$

and comparing this with (17),

$$C_1 + C_2 = 2\kappa e^2.$$

We put, therefore,

$$C_1 = e^2(\kappa + \beta),$$

$$C_2 = e^2(\kappa - \beta),$$

where  $\beta$  is a constant. Next, as in Art. 6, we write for brevity

$$f_1(\xi) = -\frac{\alpha^2}{\xi^2} - eE\xi^4 - 2A\xi^2 + 2e^2(\kappa + \beta),$$

$$f_2(\eta) = -\frac{\alpha^2}{\eta^2} + eE\eta^4 - 2A\eta^2 + 2e^2(\kappa - \beta).$$

Thus we get

$$m(\xi^2 + \eta^2)\dot{\xi} = \sqrt{mf_1(\xi)}, \quad . \quad . \quad (22)$$

$$m(\xi^2 + \eta^2)\dot{\eta} = \sqrt{mf_2(\eta)}, \quad . \quad . \quad (23)$$

where, of course,  $\sqrt{mf_1(\xi)}$  and  $\sqrt{mf_2(\eta)}$  must have the same signs as  $\xi$  and  $\eta$  respectively. The left-hand members represent the momenta.

The integration is now easily accomplished. In fact, from (22) and (23) we have

$$\frac{d\xi}{\sqrt{f_1(\xi)}} - \frac{d\eta}{\sqrt{f_2(\eta)}} = 0,$$

so that

$$\int \frac{d\xi}{\sqrt{f_1(\xi)}} - \int \frac{d\eta}{\sqrt{f_2(\eta)}} = \beta'. \quad (24)$$

Again,

$$\frac{\dot{\xi}}{\sqrt{f_1(\xi)}} = \frac{1}{\sqrt{m(\xi^2 + \eta^2)}}, \quad \frac{\dot{\eta}}{\sqrt{f_2(\eta)}} = \frac{1}{\sqrt{m(\xi^2 + \eta^2)}},$$

$$\frac{\xi^2 \dot{\xi}}{\sqrt{f_1(\xi)}} + \frac{\eta^2 \dot{\eta}}{\sqrt{f_2(\eta)}} = \frac{1}{\sqrt{m}},$$

$$\int \frac{\xi^2 d\xi}{\sqrt{f_1(\xi)}} + \int \frac{\eta^2 d\eta}{\sqrt{f_2(\eta)}} = \frac{1}{\sqrt{m}}(t - t_0), \quad (25)$$

$$\frac{\dot{\xi}}{\xi^2 \sqrt{f_1(\xi)}} + \frac{\dot{\eta}}{\eta^2 \sqrt{f_2(\eta)}} = \frac{1}{\sqrt{m(\xi^2 + \eta^2)}} \left( \frac{1}{\xi^2} + \frac{1}{\eta^2} \right) = \frac{1}{\sqrt{m\xi^2 \eta^2}} = \frac{1}{\alpha} \dot{\phi},$$

$$\int \frac{d\xi}{\xi^2 \sqrt{f_1(\xi)}} + \int \frac{d\eta}{\eta^2 \sqrt{f_2(\eta)}} = \frac{1}{\alpha}(\phi - \phi_0). \quad (26)$$

We have thus found again the equations derived at the end of Art. 6, containing the six constants

$$A, \alpha, \beta, \beta', t_0, \phi_0.$$

(24) determines the orbit in the rotating plane,

(25) determines the time of passage of the electron through a given point of that plane,

(26) determines the angle which that plane makes with its own initial position when the electron occupies in it a given place.

We will now consider the physical significance of the co-ordinates  $\xi$  and  $\eta$ . These are defined by the equations

$$r = \frac{1}{2}(\xi^2 + \eta^2), \quad x = \frac{1}{2}(\xi^2 - \eta^2)$$

which can also be written

$$\xi^2 = r + x, \quad \eta^2 = r - x.$$

The equation  $r - x = \eta^2 = \text{const.}$  says that the distances from  $O$  and from a straight line  $AB \perp OX$  are equal. Similarly,

$r + x = \xi^2 = \text{const.}$  says that the distances from  $O$  and another straight line  $A'B' \perp OX$  are equal. Thus the lines  $\xi = \text{const.}$  and  $\eta = \text{const.}$  are parabolae whose common focus is  $O$  and whose

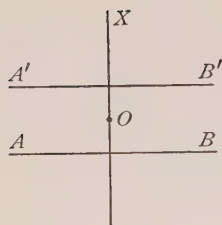


FIG. 3.

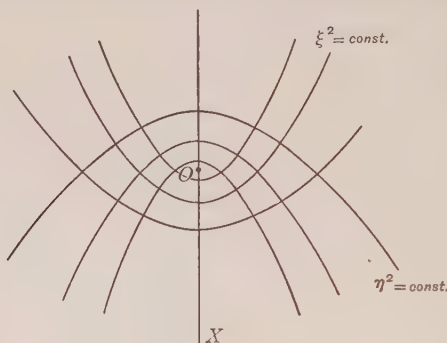


FIG. 4.

concave sides are turned in opposite directions (Fig. 4). It can readily be proved that the two systems of parabolae cut each other orthogonally, which follows already from the fact that  $\xi + i\eta$  is a function of  $x + iy$  alone.

Similarly as in the absence of an electric field, there are now two kinds of possible motions, such in which  $\xi$  and  $\eta$  increase indefinitely, and such in which each of these variables lies between given limits without ever exceeding them. The latter case, to which we can confine our attention, occurs if  $f_1(\xi)$  vanishes for two values  $\xi_1$  and  $\xi_2$  and remains positive between them, and if

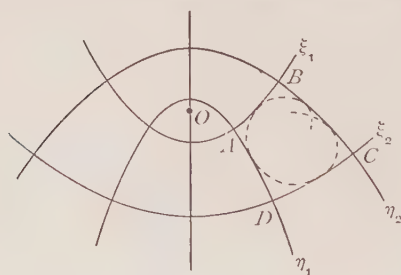


FIG. 5.

$f_2(\eta)$  behaves similarly between  $\eta_1$  and  $\eta_2$ . We then have a possible motion during which  $\xi$  and  $\eta$  remain always within these limits, that is to say, a motion in the [rotating] meridian plane confined to a quadrangle formed by two  $\xi$ -lines and two  $\eta$ -lines.

Such a quadrangle is  $ABCD$  in Fig. 5, where the dotted line indicates a possible motion. We take  $\xi_1 < \xi_2$ . While  $\xi$  passes from  $\xi_1$  to  $\xi_2$ ,  $\sqrt{mf_1(\xi)}$  must be taken with the positive sign, and

for the inverse passage with the negative sign. Also in the remaining integrals the signs of  $\sqrt{f_1(\xi)}$  and  $\sqrt{f_2(\eta)}$  must be properly chosen. Thus, *e.g.*, in (24) both  $\frac{d\xi}{\sqrt{f_1(\xi)}}$  and  $\frac{d\eta}{\sqrt{f_2(\eta)}}$  must be positive.

Let us see how the path of the electron can be found from (24). Move along  $AD$  back and forth and mark at each point  $P$  attained the value of the integral

$$I_1 = \int_A^P \left| \frac{d\xi}{\sqrt{f_1(\xi)}} \right|.$$

The number  $I_1$  is zero at  $A$ , increases towards  $D$ , where it attains a certain value  $s_1$ , continues to increase on the way back in the same manner, so that it reaches the value  $2s_1$  at  $A$ , and then undergoes the same changes as before. Thus, if  $\sigma_1$  is the first value attained at a point  $P$ , the second value is  $2s_1 - \sigma_1$ , the third  $2s_1 + \sigma_1$ , and so on, so that we have at this point the two series of values

$$\begin{aligned} \sigma_1, \sigma_1 + 2s_1, \sigma_1 + 4s_1, \dots \\ -\sigma_1 + 2s_1, -\sigma_1 + 4s_1, -\sigma_1 + 6s_1, \dots \end{aligned}$$

Similarly, the numbers

$$\begin{aligned} \sigma_2, \sigma_2 + 2s_2, \sigma_2 + 4s_2, \dots \\ -\sigma_2 + 2s_2, -\sigma_2 + 4s_2, \dots \end{aligned}$$

will belong to the points of  $AB$ . Now, the value of  $\beta'$  in (24) being chosen, we can choose a number on  $AD$  and one on  $AB$ , which is smaller by  $\beta'$ . We then find a point on  $AD$  and one on  $AB$ , and if we draw through these points a  $\xi$ -line and an  $\eta$ -line, the cross of these lines will be a point of the path. This path resembles somewhat Lissajou's figures. The constant  $\beta'$  can be compared with a phase difference. If  $\beta'$  is increased or decreased by  $2s_1$  or  $2s_2$ , we get again the same path.

If  $s_1 = s_2$ , the path closes after a single circumvolution.

More generally, if  $s_1$  and  $s_2$  are commensurable, the path is closed after several circumvolutions.

Finally, if  $s_1$  and  $s_2$  are incommensurable, the path is not closed.

As regards (25) and (26), it may be well to note that the constants  $t_0$  and  $\phi_0$  have nothing to do with the type of the motion.

Having now obtained a good insight into the meaning of  $\xi$  and  $\eta$  we can pass to the quantum conditions. We know that the dimensions of  $h$  are those of an energy multiplied by a time. Now, it is well-known that, no matter how the co-ordinates  $q$  are chosen, the corresponding momenta are given by  $\partial T/\partial \dot{q}$ . Thus the product of a velocity  $\dot{q}$  into the corresponding momentum has the dimensions of an energy, and the time integral of such a product,  $\int p \dot{q} dt$ , the dimensions of  $h$ . This integral can also be written  $\int p dq$ , to be extended over any time interval. Matters become most simple when the momentum corresponding to a co-ordinate  $q$  can be expressed as a function of this co-ordinate. Then the integral  $\int p dq$  can be evaluated provided that its limits are functions of the integration constants of the problem. But such is exactly the case of the components of momentum corresponding to  $\xi$  and  $\eta$ ,  $m(\xi^2 + \eta^2)\dot{\xi}$  and  $m(\xi^2 + \eta^2)\dot{\eta}$ , which are expressed by (22) and (23) in terms of  $\xi$  and  $\eta$ .

Now, Epstein assumes that these momenta, multiplied by  $d\xi$  and  $d\eta$  and integrated for a complete passage back and forth between the aforesaid limits, are exact multiples of  $h$ , thus :

$$2 \int_{\xi_1}^{\xi_2} \sqrt{mf_1(\xi)} d\xi = n_1 h, \quad 2 \int_{\eta_1}^{\eta_2} \sqrt{mf_2(\eta)} d\eta = n_2 h.$$

The momentum corresponding to  $\phi$  is  $\sqrt{m}a$ . This multiplied by  $d\phi$  and integrated over a full period  $2\pi$ , is again equated to a multiple of  $h$ . Thus,

$$2\pi\sqrt{m}a = n_3 h.$$

The "momentum" corresponding to the angular co-ordinate  $\phi$  is what we commonly call the moment of momentum. The latter is thus, as in Bohr's case,  $n_3 h/2\pi$ .

Before proceeding with our subject let us consider a linear vibrator. Here we have to do only with one condition. What does it amount to ?

The vibrations can be expressed by

$$q = a \cos 2\pi\nu t,$$

whence

$$\dot{q} = -2\pi\nu a \sin 2\pi\nu t,$$

$$p = m\dot{q} = -2\pi\nu am \sin 2\pi\nu t = -2\pi\nu am \sqrt{1 - \frac{q^2}{a^2}}.$$



By what precedes we have to take as the quantum condition

$$2 \int_{-a}^{+a} 2\pi\nu am \sqrt{1 - \frac{q^2}{a^2}} dq = nh$$

or 
$$4\pi\nu a^2 m \int_{-1}^{+1} \sqrt{1 - u^2} du = nh,$$

and since the value of the integral is  $\pi/2$ ,

$$2\pi^2\nu a^2 m = nh.$$

Thus we have for the energy

$$\frac{1}{2}ma^2 \cdot 4\pi^2\nu^2 = 2\pi^2\nu^2 a^2 m = n\nu h,$$

the known condition for a linear vibrator.

Let us now return to Epstein's case.\*

To find the limits of  $\xi$  and  $\eta$ , between which the integrals appearing in the quantum conditions have to be taken, we introduce new variables through  $\xi^2 = u$ ,  $\eta^2 = v$ .

This gives

$$f_1(\xi) = \frac{2A}{u} [pu^3 - (u - q)(u - r)],$$

$$f_2(\eta) = \frac{2A}{v} [pv^3 - (v - \bar{q})(v - \bar{r})],$$

where

$$p = -\frac{eE}{2A}, \quad q + r = \frac{e^2}{A}(\kappa + \beta), \quad qr = \frac{a^2}{2A},$$

$$\bar{p} = \frac{eE}{2A}, \quad \bar{q} + \bar{r} = \frac{e^2}{A}(\kappa - \beta), \quad \bar{q}\bar{r} = \frac{a^2}{2A}.$$

\* Epstein's "quantizing" rule can be represented as follows:

Since  $T = \frac{1}{2} \Sigma p \dot{q}$ , half the product of the rate of change of a co-ordinate into the corresponding momentum may be called the kinetic energy belonging to that co-ordinate. Now, suppose that with an appropriate choice of the co-ordinates one of them,  $q$ , oscillates back and forth between two fixed limits  $\alpha$  and  $\beta$ . Call the passage from  $\alpha$  to  $\beta$  and back to  $\alpha$  an "oscillation." Further, suppose that the time integral of the kinetic energy belonging to the co-ordinate  $q$ , extended over an oscillation, has for the successive oscillations, the same value. Then the quantum condition is that this value shall be a multiple of  $\frac{1}{2}h$ .

Notice that the motion need not be "periodical"; while  $q$  oscillates the remaining co-ordinates need not move back and forth between fixed limits, and if they do so, they need not reach their extreme values at the same instants as  $q$ . Again, the successive oscillations of  $q$  itself may very well be of unequal duration.

The condition that the value of the above time integral shall be the same for the successive oscillations is obviously satisfied if the momentum  $p$  can be expressed in terms of the co-ordinate  $q$  alone.

Further, we can put

$$f_1(\xi) = \frac{2pA}{u}(u-u_1)(u-u_2)(u-u_3),$$

where  $u_1, u_2, u_3$  are the roots of the equation

$$pu^3 - (u-q)(u-r) = 0.$$

Since  $E$  can be assumed to be small, we have here that special case of a cubic, in which the coefficient of the third power is very small. Under these circumstances two of the three roots, say  $u_1$  and  $u_2$ , differ but little from  $q$  and  $r$ , and the third does not differ much from  $1/p$ . Thus the roots become

$$u_1 = q + \frac{q^3}{q-r}p, \quad u_2 = r + \frac{r^3}{r-q}p, \quad u_3 = \frac{1}{p} - (q+r).$$

We will now assume that  $q$  and  $r$  are real and positive. Then the same will be the case of  $u_1$  and  $u_2$ . Further, let  $u_1 < u_2$ .

We can write

$$f_1(\xi) = 2pu_3A \cdot \frac{1}{u} \left(1 - \frac{u}{u_3}\right)(u-u_1)(u_2-u)$$

or

$$f_1(\xi) = 2\{1 - (q+r)p\}A \cdot \frac{1}{u} \left(1 - \frac{u}{u_3}\right)(u-u_1)(u_2-u),$$

so that

$$\begin{aligned} \sqrt{mf_1(\xi)}d\xi &= \sqrt{\frac{mf_1(\xi)}{4u}}du \\ &= \sqrt{\frac{mA}{2}\{1 - (q+r)p\} \frac{1}{u^2} \left(1 - \frac{u}{u_3}\right)(u-u_1)(u_2-u)}du. \end{aligned}$$

This expression is to be integrated from  $u_1$  to  $u_2$  and the integral to be taken twice. Now, since throughout the interval

$$u < u_3,$$

we can put

$$\sqrt{1 - \frac{u}{u_3}} = 1 - \frac{u}{2u_3} = 1 - \frac{1}{2}up$$

and we have thus to evaluate

$$\begin{aligned} \sqrt{2mA}\{1 - \tfrac{1}{2}(q+r)p\} \int_{u_1}^{u_2} \left(1 - \frac{p}{2}\right) \sqrt{(u-u_1)(u_2-u)}du \\ = \sqrt{2mA}\{1 - \tfrac{1}{2}(q+r)p\} \int_{u_1}^{u_2} \frac{1}{u} \sqrt{(u-u_1)(u_2-u)}du \\ - \tfrac{1}{2}\sqrt{2mA}p \int_{u_1}^{u_2} \sqrt{(u-u_1)(u_2-u)}du. \quad (27) \end{aligned}$$

[\* The term containing  $p^2$  being neglected.]

The two integrals appearing in this expression can now be determined separately. The indefinite integrals are

$$\begin{aligned} \int \frac{1}{u} \sqrt{(u-u_1)(u_2-u)} du &= \sqrt{(u-u_1)(u_2-u)} \\ &+ \frac{1}{2}(u_1+u_2) \arcsin \frac{2u-(u_1+u_2)}{u_2-u_1} \\ &+ \sqrt{u_1 u_2} \arcsin \frac{-(u_1+u_2)u+2u_1 u_2}{(u_2-u_1)u} \end{aligned}$$

$$\begin{aligned} \int \sqrt{(u-u_1)(u_2-u)} du &= \frac{1}{4}\{2u-(u_1+u_2)\} \sqrt{(u-u_1)(u_2-u)} \\ &+ \frac{1}{8}(u_2-u_1)^2 \arcsin \frac{2u-(u_1+u_2)}{u_2-u_1}. \end{aligned}$$

Taking these integrals between the limits  $u_1$  and  $u_2$  and noticing that

$$\frac{2u-(u_1+u_2)}{u_2-u_1} = \mp 1 \text{ for } u = \frac{u_1}{u_2}$$

and

$$\frac{-(u_1+u_2)u+2u_1 u_2}{(u_2-u_1)u} = \pm 1 \text{ for } u = \frac{u_1}{u_2},$$

we find

$$\begin{aligned} \int_{u_1}^{u_2} \frac{1}{u} \sqrt{(u-u_1)(u_2-u)} du &= \frac{1}{2} \pi (u_1+u_2) - \pi \sqrt{u_1 u_2} = \frac{1}{2} \pi (\sqrt{u_2} - \sqrt{u_1})^2, \\ \int_{u_1}^{u_2} \sqrt{(u-u_1)(u_2-u)} du &= \frac{1}{8} \pi (u_2-u_1)^2. \end{aligned}$$

Here we substitute, always neglecting terms with  $p^2$ ,

$$\begin{aligned} u_1 &= q + \frac{q^3}{q-r} p, & u_2 &= r + \frac{r^3}{r-q} p, \\ u_1 + u_2 &= q + r + \frac{q^3 - r^3}{q-r} p = q + r + (q^2 + qr + r^2)p, \\ u_1 u_2 &= qr + \frac{q^3 r - q r^3}{q-r} p = qr + (q+r)qr p, \\ \sqrt{u_1 u_2} &= \sqrt{qr} + \frac{1}{2}(q+r)\sqrt{qr} p. \end{aligned}$$

Thus the first integral becomes

$$\begin{aligned} \int_{u_1}^{u_2} \frac{1}{u} \sqrt{(u-u_1)(u_2-u)} du &= \frac{\pi}{2} \{(q+r) - 2\sqrt{qr} \\ &+ [(q^2 + qr + r^2) - (q+r)\sqrt{qr}]p\}. \end{aligned}$$

In the second integral which appears in (27) with the factor  $p$  the terms containing  $p$  can be neglected, so that

$$\int_{u_1}^{u_2} \sqrt{(u-u_1)(u_2-u)} du = \frac{\pi}{8}(r-q)^2.$$

With these values we have now to calculate the integral of  $\sqrt{mf_1(\xi)}d\xi$ , *i.e.* the expression (27).

Now, the first integral multiplied by  $\{1 - \frac{1}{2}(q+r)p\}$  gives, after the rejection of the  $p^2$  term,

$$\frac{1}{2}\pi\{(q+r) - 2\sqrt{qr} + \frac{1}{2}(q^2+r^2)p\}.$$

To this we have to add the second integral multiplied by  $-\frac{1}{2}p$ , *i.e.*

$$\frac{1}{2}\pi(-\frac{1}{8}q^2 + \frac{1}{4}qr - \frac{1}{8}r^2)p.$$

This gives

$$\frac{\pi}{2}\{(q+r) - 2\sqrt{qr} + (\frac{3}{8}q^2 + \frac{1}{4}qr + \frac{3}{8}r^2)p\}.$$

Thus the first quantum condition becomes

$$\frac{\pi}{2}\sqrt{2mA}\{(q+r) - 2\sqrt{qr} + (\frac{3}{8}q^2 + \frac{1}{4}qr + \frac{3}{8}r^2)p\} = n_1 h$$

or

$$\sqrt{\frac{mA}{2}}[q+r-2\sqrt{qr}] + \frac{1}{8}\{3(q+r)^2-4qr\}p = n_1 \frac{h}{\pi}.$$

Notice that  $q$  and  $r$  (as well as  $u_1$  and  $u_2$ ) are positive and that  $\sqrt{qr}$  is to be taken with the positive sign. Now (p. 303),

$$q+r = \frac{e^2}{A}(\kappa+\beta), \quad qr = \frac{\alpha^2}{2A}, \quad p = -\frac{eE}{2A},$$

so that the first of the three quantum conditions ultimately becomes

$$\begin{aligned} \sqrt{\frac{1}{2}mA} \left\{ \frac{e^2}{A}(\kappa+\beta) - \alpha \sqrt{\frac{2}{A}} \right\} \\ - \frac{1}{16}eE \sqrt{\frac{m}{2A}} \left\{ \frac{3e^4(\kappa+\beta)^2}{A^2} - \frac{2\alpha^2}{A} \right\} = n_1 \frac{h}{\pi}. \end{aligned} \quad (28)$$

Similarly, the second condition will be found to be

$$\begin{aligned} \sqrt{\frac{1}{2}mA} \left\{ \frac{e^2}{A}(\kappa-\beta) - \alpha \sqrt{\frac{2}{A}} \right\} \\ + \frac{1}{16}eE \sqrt{\frac{m}{2A}} \left\{ \frac{3e^4(\kappa-\beta)^2}{A^2} - \frac{2\alpha^2}{A} \right\} = n_2 \frac{h}{\pi}, \end{aligned} \quad (29)$$

and the third condition,

$$2\sqrt{m\alpha} = n_3 \frac{h}{\pi}. \quad (30)$$

It remains to eliminate  $\alpha$  and  $\beta$  and thus to express the energy  $-A$  in terms of  $n_1, n_2, n_3$ .

First of all we can substitute in the second term of (28) and (29) that value of  $\beta$ , say  $\beta_0$ , which corresponds to  $E=0$ . This is permissible because the terms containing  $E$  are small.

Now, the equations determining  $\beta_0$  are

$$e^2 \sqrt{\frac{m}{2A}} (\kappa + \beta_0) - n_3 \frac{h}{2\pi} = n_1 \frac{h}{\pi},$$

$$e^2 \sqrt{\frac{m}{2A}} (\kappa - \beta_0) - n_3 \frac{h}{2\pi} = n_2 \frac{h}{\pi},$$

whence

$$(\kappa + \beta_0) : (\kappa - \beta_0) = (n_1 + \frac{1}{2}n_3) : (n_2 + \frac{1}{2}n_3),$$

$$\kappa : \beta_0 = (n_1 + n_2 + n_3) : (n_1 - n_2).$$

Next, adding (28) and (29), we have

$$e^2 \sqrt{\frac{2m}{A}} \kappa = (n_1 + n_2 + n_3) \frac{h}{\pi} + \frac{3}{4} e^5 \kappa \beta_0 E \sqrt{\frac{m}{2A^5}},$$

and writing this in the form

$$\frac{\lambda}{\sqrt{A}} = \mu + \frac{\sigma}{\sqrt{A^5}},$$

we find for the energy

$$-A = -\frac{\lambda^2}{\mu^2} + \frac{2\sigma\mu^2}{\lambda^3}.*$$

Here

$$\lambda = e^2 \kappa \sqrt{2m}, \quad \mu = (n_1 + n_2 + n_3) \frac{h}{\pi},$$

$$\sigma = \frac{3}{4} e^5 E \kappa^2 (n_1 - n_2) (n_1 + n_2 + n_3)^{-1} \sqrt{\frac{m}{2}},$$

so that, ultimately,

$$-A = -(n_1 + n_2 + n_3)^{-2} \frac{2\pi^2 m e^4 \kappa^2}{h^2} + \frac{3}{8} (n_1 - n_2) (n_1 + n_2 + n_3) \frac{h^2}{\pi^2 m e \kappa} E.$$

---

\* Since  $\sigma$  is small,  $1/\sqrt{A}$  in the second term of the last equation can be replaced by  $\mu/\lambda$ ; thus the equation becomes  $\frac{1}{\sqrt{A}} = \frac{\mu}{\lambda} \left( 1 + \sigma \frac{\mu^4}{\lambda^5} \right)$ , whence, neglecting the second and higher powers of  $\lambda$ , the above given value of  $-A$  is obtained.

Thus, when the electron passes from  $n_1, n_2, n_3$  to  $n'_1, n'_2, n'_3$ , the vibration frequency of the emitted radiation is

$$\nu = \left\{ \frac{1}{(n'_1 + n'_2 + n'_3)^2} - \frac{1}{(n_1 + n_2 + n_3)^2} \right\} \frac{2\pi^2 m e^4 \kappa^2}{h^3} + \frac{3}{8} \{ (n_1 - n_2)(n_1 + n_2 + n_3) - (n'_1 - n'_2)(n'_1 + n'_2 + n'_3) \} \frac{h}{\pi^2 m e \kappa} E. \quad (31)$$

The coefficient of the first term is identical with that of  $(1/p'^2 - 1/p^2)$  in Balmer's formula (p. 281),  $2\pi^2 m e^2 E^2 / h^3 = 2\pi^2 m e^4 \kappa^2 / h^3$ , the charge of the nucleus for which we have previously written  $E$  being now denoted by  $e\kappa$ .

Formula (31) coincides exactly with Epstein's result, apart from the factor  $c$  in the denominator. This is due to the circumstance that Epstein writes  $\nu$  not for the number of vibrations per second, *i.e.*  $c/\lambda$ , but for the wave-number  $1/\lambda$ .

Let us denote the second term of (31), which expresses the effect of the electric field, by  $\Delta\nu$  and the corresponding change in wave-length ( $\lambda = c/\nu$ ) by  $\Delta\lambda$ , so that [apart from signs]

$$\Delta\lambda = \frac{c}{\nu^2} \Delta\nu = \frac{\lambda^2}{c} \Delta\nu,$$

and let us put for brevity

$$(n_1 - n_2)(n_1 + n_2 + n_3) - (n'_1 - n'_2)(n'_1 + n'_2 + n'_3) = Z.$$

Then

$$\Delta\lambda = \frac{3h\lambda^2}{8\pi^2 m e c \kappa} E Z.$$

The numbers  $n_1 + n_2 + n_3$  and  $n'_1 + n'_2 + n'_3$  in the first term of (31) play the same rôle as  $p$  and  $p'$  in our previous Balmer formula. For the hydrogen line  $H_\alpha$

$$n_1 + n_2 + n_3 = 3, \quad n'_1 + n'_2 + n'_3 = 2,$$

and these sums can be obtained by attributing different values to the addends. This gives a number of possible  $Z$ -values, and since to each of these corresponds a certain  $\Delta\lambda$ , the spectrum line will be split into as many components.

That the separation of the components is proportional to the field intensity  $E$ , is manifest. Again, the splitting is symmetrical, since a permutation of  $n_1$  with  $n_2$  and of  $n'_1$  with  $n'_2$  does not alter the values of the sums, so that  $Z$  retains its absolute value and changes its sign.



Similar relations hold for the lines  $H_{\beta}$ ,  $H_{\gamma}$ , etc. But since for these lines the sum  $n_1 + n_2 + n_3$  has the values 4, 5, etc., and since a great integer can be decomposed into three integers in more ways than a small one, the number of  $Z$ -values will become greater and greater. Thus the experimental fact that the number of components increases, when we pass to higher and higher members of the spectrum series, is accounted for in a remarkably simple way.

For each line the coefficient of  $Z$  in the formula for  $\Delta\lambda$  can be completely calculated. Epstein carries out this calculation for the field intensity of 104,000 volts per cm., as applied in Stark's experiments. Since our units are the usual electrostatic ones, we have to put

$$E = \frac{104,000 \cdot 10^8}{3 \cdot 10^{10}} = 347.$$

Again, for hydrogen,  $\kappa=1$ , and  $e=4.77 \cdot 10^{-10}$ ,  $e/m=5.31 \cdot 10^{17}$ ,  $h=6.547 \cdot 10^{-27}$ . Thus for  $H_{\alpha}$  ( $\lambda=6.565 \cdot 10^{-5}$  cm.) the formula gives  $\Delta\lambda=2.89 \cdot 10^{-8} Z$  cm. or  $2.89 Z$  Ångström units. (Epstein has  $2.94 Z$ .)

To see how closely Stark's results are represented by Epstein's theory it is enough to mention that for the line  $H_{\delta}$ , for instance,  $Z$  can have all even values from 0 up to 32, inclusively, and that to

$$Z=20, 22, 24, 26, 28$$

correspond the theoretical separations  $\Delta\lambda$

$$23.8, 26.2, 28.6, 30.9, 33.4,$$

while the observed ones are

$$24.2, 25.8, 28.6, 30.4, 33.4.$$

In conclusion let us still consider the passage to the case  $E=0$ , for which one gets, of course, the usual elliptic motion.

To simplify matters, let us take the case in which the electron moves in a plane parallel to the direction of  $E$ , so that, by (14),  $a=0$ . Then

$$\begin{aligned} \int_{\xi_1}^{\xi_2} \frac{d\xi}{\sqrt{f_1(\xi)}} &= \int_{\sqrt{q}}^{\sqrt{r}} \sqrt{\frac{u}{2A}} \cdot \frac{d\xi}{\sqrt{(u-q)(r-u)}} \\ &= \frac{1}{2\sqrt{2A}} \int_q^r \frac{du}{\sqrt{(u-q)(r-u)}} = \frac{\pi}{2\sqrt{2A}}, \end{aligned}$$

and similarly

$$\int_{\eta_1}^{\eta_2} \frac{d\eta}{\sqrt{f_2(\eta)}} = \frac{\pi}{2\sqrt{2A}}.$$

From the equality of these two integrals it follows that the path closes after a single circumvolution (cf. p. 301).

Since now  $\alpha = 0$  and  $E = 0$ , the quantum conditions become

$$\sqrt{\frac{m}{2}A} \frac{e^2}{A} (\kappa + \beta) = n_1 \frac{h}{\pi},$$

$$\sqrt{\frac{m}{2}A} \frac{e^2}{A} (\kappa - \beta) = n_2 \frac{h}{\pi}.$$

To find the orbit equation in an integral form we put

$$\frac{e^2(\kappa + \beta)}{A} = f^2, \quad \frac{e^2(\kappa - \beta)}{A} = g^2.$$

Then  $f_1(\xi) = 2A(f^2 - \xi^2)$ ,  $f_2(\eta) = 2A(g^2 - \eta^2)$ ,  
and equation (24) becomes

$$\int \frac{d\xi}{\sqrt{f^2 - \xi^2}} - \int \frac{d\eta}{\sqrt{g^2 - \eta^2}} = \beta' \sqrt{2A} = C$$

or, integrated,

$$\arcsin \frac{\xi}{f} - \arcsin \frac{\eta}{g} = C.$$

If we put  $\sin \psi = \frac{\xi}{f}$ ,  $\sin \chi = \frac{\eta}{g} = \sin (\psi - C)$ , this can be written

$$\frac{\eta}{g} = \frac{\xi}{f} \cos C - \sqrt{1 - \frac{\xi^2}{f^2}} \sin C,$$

$$\frac{\eta^2}{g^2} - 2 \frac{\xi \eta}{gf} \cos C + \frac{\xi^2}{f^2} = \sin^2 C$$

or, in rectangular co-ordinates, (cf. p. 295)

$$\frac{r-x}{g^2} - \frac{2y}{fg} \cos C + \frac{r+x}{f^2} = \sin^2 C.$$

This equation gives  $r$  as a linear function of  $x$  and  $y$  and represents, therefore, an ellipse.

Do Epstein's quantum conditions lead in the limit to those of Bohr?

The moment of momentum in the plane of the orbit is

$$m(xy - y\dot{x}) = \frac{1}{2} m(\xi^2 + \eta^2)(\xi \dot{\eta} - \eta \dot{\xi}) = \frac{1}{2} (\xi \sqrt{mf_2(\eta)} - \eta \sqrt{mf_1(\xi)})$$

$$= \frac{1}{2} \sqrt{mfg} \sqrt{2A} (\sin \psi \cos \chi - \cos \psi \sin \chi) = \frac{1}{2} \sqrt{mfg} \sqrt{2A} \sin C.$$

Since, according to Epstein (cf. top of this page),

$$\sqrt{\frac{1}{2}mAf^2} = n_1 \frac{h}{\pi} \quad \text{and} \quad \sqrt{\frac{1}{2}mAg^2} = n_2 \frac{h}{\pi},$$

we have

$$\sqrt{\frac{1}{2}m}Afg = \sqrt{n_1 n_2} \frac{h}{\pi},$$

so that the moment of momentum becomes

$$\sqrt{n_1 n_2} \sin C \cdot \frac{h}{\pi}.$$

Now, this is no exact multiple of  $h/2\pi$ . Yet, and this is very remarkable, the expression found on p. 307 for the energy  $-A$  reduces for  $E=0$  to that derived by Bohr. Thus also Balmer's formula reappears in Epstein's theory, as, of course, it should, for  $E=0$ .

## 8. RELATIVISTIC THEORY OF MOTION OF AN ELECTRON IN THE ATOM. SOMMERFELD'S EXPLANATION OF THE FINE STRUCTURE OF SPECTRUM LINES

Many spectrum lines are known to be fine doublets or triplets. Of this multiplicity of the lines Sommerfeld succeeded in giving a particularly beautiful explanation by applying the fundamental formulae of relativistic mechanics. He had good reasons for doing so, since in many cases the velocities of the revolving electrons are not negligibly small compared with the velocity of light. The considerations of pp. 287-289 can again be applied, only that, putting

$$H = \int_{t_0}^t L dt,$$

we now have to take for  $L$ , instead of  $\frac{1}{2}mv^2 - U$ ,

$$L = -mc^2(\sqrt{1-v^2/c^2} - 1) - U, \quad . \quad . \quad . \quad (32)$$

an expression which for small velocities  $v$  reduces to the previous one.

If the position of the electron is determined by the co-ordinates  $q_1, q_2, q_3$ , then  $L$  is a function of these and of  $\dot{q}_1, \dot{q}_2, \dot{q}_3$ , and passing to a varied motion (cf. p. 287), one finds

$$\begin{aligned} \delta L &= \sum \left[ \frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \delta \dot{q} \right] = \sum \left[ \frac{\partial L}{\partial q} \delta q + \frac{\partial L}{\partial \dot{q}} \frac{d \delta q}{dt} \right] - \frac{d \delta t}{dt} \sum \dot{q} \frac{\partial L}{\partial \dot{q}} \\ &= \frac{d}{dt} \sum \frac{\partial L}{\partial \dot{q}} \delta q + \sum \left[ \frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} \right] \delta q - \frac{d \delta t}{dt} \sum \dot{q} \frac{\partial L}{\partial \dot{q}}, \end{aligned}$$

whence

$$\begin{aligned}\delta H &= \int_{t_0}^t \delta L dt + \int_{t_0}^t L d\delta t \\ &= \int_{t_0}^t \sum \left\{ \frac{\partial L}{\partial q} - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) \right\} \delta q dt + \int_{t_0}^t \left( L - \sum \dot{q} \frac{\partial L}{\partial \dot{q}} \right) d\delta t + \left| \sum p \delta q \right|_{t_0}^t, \quad (33)\end{aligned}$$

where we have put

$$\frac{\partial L}{\partial \dot{q}} = p. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

For a natural motion we require  $\delta H = 0$ , the time and the initial and the final states not being varied. This gives the three equations of motion

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_1} \right) - \frac{\partial L}{\partial q_1} = 0, \text{ etc.}$$

Multiplying these by  $\dot{q}_1$ , etc., and adding, we have

$$\begin{aligned}\sum \left[ \dot{q} \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) - \dot{q} \frac{\partial L}{\partial q} \right] &= \frac{d}{dt} \sum \dot{q} \frac{\partial L}{\partial \dot{q}} - \sum \left( \dot{q} \frac{\partial L}{\partial \dot{q}} + \dot{q} \frac{\partial L}{\partial \dot{q}} \right) \\ &= \frac{d}{dt} \left\{ \sum \left( \dot{q} \frac{\partial L}{\partial \dot{q}} \right) - L \right\} = 0,\end{aligned}$$

whence we see that

$$\sum \left( \dot{q} \frac{\partial L}{\partial \dot{q}} \right) - L \quad . \quad . \quad . \quad . \quad . \quad (35)$$

does not change during the motion. This is the energy, as will be seen by considering the special case of small velocities. In fact, then

$$L = \frac{1}{2}mv^2 - U,$$

so that, using rectangular co-ordinates, the expression (35) reduces to  $\frac{1}{2}mv^2 + U$ .

Thus, if  $A$  has the same meaning as before,

$$A = L - \sum \dot{q} \frac{\partial L}{\partial \dot{q}} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The magnitudes  $p$  determined by (34) are the momenta. In the simple case just mentioned they have, in fact, the values  $m\dot{x}$ ,  $m\dot{y}$ ,  $m\dot{z}$ .

If the original motion is a natural one, the general equation (33) passes, in virtue of the equations of motion, as before (p. 288) into

$$\delta H = A \delta(t - t_0) + \left| \sum p \delta q \right|_{t_0}^t.$$

Also for a non-natural motion  $A$  can be defined by (36) and we can put for any motion, whether natural or not,

$$W = H - A(t - t_0).$$

This then will be the action, and the principle of least action will again hold. In fact, if the original motion is a natural one (so that during this motion  $A$  remains constant), then, leaving the terminal states unaltered and adjusting the velocity along the varied path in such a manner that  $A$  shall have the same value as in the original motion, we have

$$\delta W = 0.$$

If the original natural motion is so varied as to remain natural and the initial state is not altered, the corresponding variation of  $W$  will again be given by the formula on p. 289, just preceding (3), and if  $W$  is considered as a function of the end-co-ordinates and of the energy  $-A$ , the equations (3) and (4) remain in force.

Finally, a partial differential equation for  $W$  can again be set up. To fix the ideas, let us imagine that for the natural motions in question not only the initial state but also the energy  $-A$  is assigned. Then we get the required differential equation starting from  $L$  as a function of  $q$  and  $\dot{q}$ , expressing the momenta  $p$ , by means of (34), in terms of these magnitudes, further solving the three equations thus obtained for the velocities  $\dot{q}$ , so that they are expressed in terms of  $q$  and  $p$ , substituting these  $\dot{q}$  into (36) and, lastly, replacing the momenta  $p$  by the derivatives  $\partial W / \partial q$ .

This will now be worked out in rectangular co-ordinates  $x, y, z$ . From (32) and (34) follows

$$p_x = \frac{m\dot{x}}{\sqrt{1-v^2/c^2}}, \quad p_y = \frac{m\dot{y}}{\sqrt{1-v^2/c^2}}, \quad p_z = \frac{m\dot{z}}{\sqrt{1-v^2/c^2}},$$

$$-A = mc^2 \left( \frac{1}{\sqrt{1-v^2/c^2}} - 1 \right) + U, \quad . \quad . \quad (37)$$

where the first term of the right hand member can be called the kinetic energy.

In the variation implied in the principle of least action  $W$  can (by p. 289) be replaced by

$$H - \int_{t_0}^t A dt = \int_{t_0}^t (L - A) dt = \int_{t_0}^t \frac{mv^2}{\sqrt{1-v^2/c^2}} dt = \int \frac{mv}{\sqrt{1-v^2/c^2}} ds.$$

To arrive at the differential equation for  $W$ , we take the sum of the squares of the expressions for  $p_x, p_y, p_z$ . This gives

$$p_x^2 + p_y^2 + p_z^2 = \frac{m^2 v^2}{1 - v^2/c^2}$$

or, if we put for brevity  $p_x^2 + p_y^2 + p_z^2 = Q$ ,

$$\frac{1}{1 - v^2/c^2} = 1 + \frac{Q}{m^2 c^2}.$$

Thus formula (37) becomes

$$-mc^2 + mc^2 \sqrt{1 + \frac{Q}{m^2 c^2}} = -A - U \quad . \quad . \quad (38)$$

This, with the substitution

$$Q = \left(\frac{\partial W}{\partial x}\right)^2 + \left(\frac{\partial W}{\partial y}\right)^2 + \left(\frac{\partial W}{\partial z}\right)^2, \quad . \quad . \quad . \quad (39)$$

is the required differential equation for  $W$ .

An arbitrary solution of this equation represents the action reckoned, not from a point, but from any surface from which the electron starts in a normal direction. Again, if the solution contains a constant  $c$ , the derivative  $\partial W/\partial c$  remains constant along a path. Thus also, if we have a solution containing a sufficient number (viz. two) of non-additive constants, we can find the equations of a path by equating the derivatives with respect to these constants to new constants. Lastly, equation (10) tells us how such a path is described in the course of time. These statements can be proved by much the same reasoning as on pp. 291-293, and need not, therefore, detain us here any further.

All this holds also, if instead of  $x, y, z$  other co-ordinates  $q_1, q_2, q_3$  are introduced. The partial differential equation can then be obtained either by using the new co-ordinates from the outset or, more simply, by introducing them as independent variables into (39).

Let us now proceed with our subject. Sommerfeld considers the case of an electron  $-e$  revolving around a positively charged nucleus and subjected to no other force than the attraction by the nucleus. It is clear that under these circumstances the electron describes a plane orbit, so that we have to do only with two co-ordinates in the plane. Let these be the rectangular co-ordinates  $x, y$ , with the origin placed at the nucleus. Then the



only change to be made in the preceding formulae consists in replacing (39) by

$$Q = \left( \frac{\partial W}{\partial x} \right)^2 + \left( \frac{\partial W}{\partial y} \right)^2.$$

It is preferable, however, to introduce polar co-ordinates  $r, \phi$  through

$$x = r \cos \phi, \quad y = r \sin \phi.$$

Then

$$Q = \left( \frac{\partial W}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial W}{\partial \phi} \right)^2,$$

and since

$$U = -\frac{eE}{r},^*$$

formula (38) becomes

$$1 + \frac{Q}{m^2 c^2} = \left[ 1 + \frac{1}{m c^2} \left( \frac{eE}{r} - A \right) \right]^2$$

or

$$\left( \frac{\partial W}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial W}{\partial \phi} \right)^2 = m^2 c^2 \left\{ \left[ 1 + \frac{1}{m c^2} \left( \frac{eE}{r} - A \right) \right]^2 - 1 \right\}.$$

Let us denote the right-hand member, which is a function of  $r$ , by  $\rho$ , so that

$$\left( \frac{\partial W}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial W}{\partial \phi} \right)^2 = \rho.$$

A solution of this partial differential equation is

$$W = R + a\phi,$$

where  $R$  is a function of  $r$  alone, and  $a$  a constant. This gives

$$\left( \frac{dR}{dr} \right)^2 + \frac{a^2}{r^2} = \rho,$$

whence

$$R = \int \frac{dr}{r} \sqrt{r^2 \rho - a^2},$$

$$W = \int \frac{dr}{r} \sqrt{r^2 \rho - a^2} + a\phi.$$

Next, since

$$\frac{\partial W}{\partial r} = p_r, \quad \frac{\partial W}{\partial \phi} = p_\phi,$$

we have

$$p_r = \frac{1}{r} \sqrt{r^2 \rho - a^2}, \quad p_\phi = a.$$

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\* The charge of the nucleus will here be again denoted by  $E$ .

In "quantizing" we keep again to the rule followed on p. 302. Thus, if  $r_1$  and  $r_2$  be the extreme values of  $r$ , we put

$$2 \int_{r_1}^{r_2} \frac{dr}{r} \sqrt{r^2 \rho - \alpha^2} = n_1 h, \quad 2\pi\alpha = n_2 h.$$

From the value of  $\rho$  follows

$$r^2 \rho - \alpha^2 = \frac{1}{c^2} \{ (A - 2mc^2)Ar^2 + 2eE(mc^2 - A)r + (e^2 E^2 - c^2 \alpha^2) \}.$$

Now,  $mc^2 \gg |A|$ , so that the coefficient of  $r$  is positive. Since we are concerned with motions in which the distance  $r$  does not become infinite but remains between the two limits  $r_1$  and  $r_2$ , the bracketed expression must vanish for these values of  $r$ . Consequently, the coefficient of  $r^2$  and the term not containing  $r$  must be negative, that is to say,  $A$  must be positive and  $\alpha^2 > \frac{e^2 E^2}{c^2}$ .

Thus we can write

$$r^2 \rho - \alpha^2 = \left( 2m - \frac{A}{c^2} \right) A (r_2 - r)(r - r_1),$$

where we have assumed  $r_1 < r_2$ .

The values of  $r_1$  and  $r_2$  will be determined by the equations

$$r_1 + r_2 = 2eE \frac{mc^2 - A}{2mc^2 A - A^2} = \frac{eE}{A} \frac{1 - A/mc^2}{1 - A/2mc^2},$$

$$r_1 r_2 = \frac{c^2 \alpha^2 - e^2 E^2}{2mc^2 A - A^2} = \frac{\alpha^2}{2mA} \frac{1 - e^2 E^2/c^2 \alpha^2}{1 - A/2mc^2}.$$

The first quantum condition now becomes

$$2 \sqrt{2mA - \frac{A^2}{c^2}} \int_{r_1}^{r_2} \frac{dr}{r} \sqrt{(r_2 - r)(r - r_1)} = n_1 h$$

or (cf. p. 305)

$$2 \sqrt{2mA - \frac{A^2}{c^2}} \pi \left| \frac{r_1 + r_2}{2} - \sqrt{r_1 r_2} \right| = n_1 h,$$

or also

$$\frac{1}{2}(r_1 + r_2) \sqrt{2mA - \frac{A^2}{c^2}} - \alpha \sqrt{1 - \frac{e^2 E^2}{c^2 \alpha^2}} = n_1 \frac{h}{2\pi}, \quad (40)$$

and the second quantum condition is

$$\alpha = n_2 \frac{h}{2\pi}. \quad (41)$$

The energy  $-A$  has now to be expressed in terms of  $n_1$  and  $n_2$ .  
Put

$$n_1 \frac{h}{2\pi} + \alpha \sqrt{1 - \frac{e^2 E^2}{c^2 \alpha^2}} = s.$$

Then 
$$\frac{1}{2}(r_1 + r_2) \sqrt{2mA - \frac{A^2}{c^2}} = s$$

or, with the above value of  $r_1 + r_2$ ,

$$\frac{m - A/c^2}{\sqrt{2mA - A^2/c^2}} = \frac{s}{eE},$$

whence

$$(A^2 - 2mc^2 A) \left( \frac{1}{c^4} + \frac{s^2}{c^2 e^2 E^2} \right) + m^2 = 0,$$

which is a quadratic equation for  $A$ . Since  $|A| \ll mc^2$ , this gives

$$-A = mc^2 \left\{ -1 + \frac{1}{\sqrt{1 + e^2 E^2 / c^2 s^2}} \right\}.$$

The constant term  $-mc^2$  can be omitted, so that

$$-A = mc^2 \left[ 1 + \frac{e^2 E^2}{c^2 s^2} \right]^{-\frac{1}{2}}.$$

Now, 
$$s = \frac{h}{2\pi} \left\{ n_1 + n_2 \sqrt{1 - \frac{4\pi^2 e^2 E^2}{n_2^2 c^2 h^2}} \right\},$$

whence, with the abbreviation

$$a = \frac{2\pi e^2}{hc},$$

$$\frac{e^2 E^2}{c^2 s^2} = \frac{(aE/e)^2}{\{n_1 + n_2 \sqrt{1 - (aE/n_2 e)^2}\}^2}.$$

Ultimately, therefore, the energy becomes

$$-A = mc^2 \left[ 1 + \frac{(aE/e)^2}{\{n_1 + n_2 \sqrt{1 - (aE/n_2 e)^2}\}^2} \right]^{-\frac{1}{2}}.$$

To give this expression a convenient form the radical has to be developed into a series. This can be done, since the pure number  $a$ , upon which everything depends, is a small fraction. With the known values of  $e$  and  $h$  Sommerfeld finds  $a = 7.10^{-3}$ .

Putting

$$a \frac{E}{e} = b$$

and neglecting terms of a higher order than  $b^6/n_2^6$  we have

$$\sqrt{1 - \left(\frac{aE}{n_2c}\right)^2} = 1 - \frac{1}{2} \frac{b^2}{n_2^2} - \frac{1}{8} \frac{b^4}{n_2^4} - \frac{1}{16} \frac{b^6}{n_2^6},$$

whence

$$\left\{ n_1 + n_2 \sqrt{1 - \frac{b^2}{n_2^2}} \right\}^{-2} = \left\{ (n_1 + n_2) - \frac{1}{2} \frac{b^2}{n_2} - \frac{1}{8} \frac{b^4}{n_2^3} - \frac{1}{16} \frac{b^6}{n_2^5} \right\}^{-2} \\ = (n_1 + n_2)^{-2} \left\{ 1 - \frac{b^2}{2n_2(n_1 + n_2)} - \frac{b^4}{8n_2^3(n_1 + n_2)} - \frac{b^6}{16n_2^5(n_1 + n_2)} \right\}^{-2}$$

or, developing again,

$$\frac{1}{(n_1 + n_2)^2} + \frac{b^2}{n_2(n_1 + n_2)^3} + \frac{(n_1 + 4n_2)b^4}{4n_2^3(n_1 + n_2)^4} + \frac{(n_1^2 + 5n_1n_2 + 8n_2^2)b^6}{8n_2^5(n_1 + n_2)^5}.$$

Thus we find ultimately, up to terms in  $b^8$  inclusive,

$$-\frac{A}{mc^2} = \left\{ 1 + \frac{b^2}{(n_1 + n_2)^2} + \frac{b^4}{n_2(n_1 + n_2)^3} + \frac{(n_1 + 4n_2)b^6}{4n_2^3(n_1 + n_2)^4} + \frac{(n_1^2 + 5n_1n_2 + 8n_2^2)b^8}{8n_2^5(n_1 + n_2)^5} \right\}^{-2} \\ = 1 - \frac{b^2}{2(n_1 + n_2)^2} - \frac{b^4}{2n_2(n_1 + n_2)^3} - \frac{(n_1 + 4n_2)b^6}{8n_2^3(n_1 + n_2)^4} - \frac{(n_1^2 + 5n_1n_2 + 8n_2^2)b^8}{16n_2^5(n_1 + n_2)^5} \\ + \frac{3}{8} \frac{b^4}{(n_1 + n_2)^4} + \frac{3}{4} \frac{b^6}{n_2(n_1 + n_2)^5} + \frac{3}{16} \frac{(n_1 + 4n_2)b^8}{n_2^3(n_1 + n_2)^6} \\ - \frac{5}{16} \frac{b^6}{(n_1 + n_2)^6} + \frac{3}{8} \frac{b^8}{n_2^2(n_1 + n_2)^6} - \frac{15}{16} \frac{b^8}{n_2(n_1 + n_2)^7} \\ + \frac{35}{128} \frac{b^8}{(n_1 + n_2)^8}.$$

If we limit ourselves to terms in  $b^4$ , then

$$-\frac{A}{mc^2} = 1 - \frac{b^2}{2(n_1 + n_2)^2} - \frac{(4n_1 + n_2)b^4}{8n_2(n_1 + n_2)^4}.$$

Here  $n_2$  corresponds to Sommerfeld's  $n$ .

Thus, if the additive term  $mc^2$  is again omitted, the energy becomes

$$-A = -\frac{mc^2b^2}{2(n_1 + n_2)^2} \left[ 1 + \frac{b^2}{(n_1 + n_2)^2} \left\{ \frac{1}{4} + \frac{n_1}{n_2} \right\} \right] \\ = -\frac{mc^2a^2}{2(n_1 + n_2)^2} \left( \frac{E}{c} \right)^2 \left[ 1 + \frac{a^2}{(n_1 + n_2)^2} \frac{E^2}{c^2} \left\{ \frac{1}{4} + \frac{n_1}{n_2} \right\} \right].$$

Since  $a = \frac{2\pi e^2}{hc}$ , we have  $\frac{mc^2a^2}{2(n_1 + n_2)^2} \frac{E^2}{c^2} = \frac{2m\pi^2e^2E^2}{h^2(n_1 + n_2)^2}.$

This introduces into the formula for the spectrum lines the factor

$$\frac{2m\pi^2e^2E^2}{h^3},$$

i.e. Rydberg's constant which, in this simplest form, will be denoted by  $R$  [for  $E=e$ , that is].

If we retain of the series only the first term, containing  $a^2$ , we just get Balmer's formula

$$\nu = R \left[ \frac{1}{(n'_1 + n'_2)^2} - \frac{1}{(n_1 + n_2)^2} \right].$$

But owing to the application of relativistic mechanics some new features are introduced. If of the second or  $a^4$ -term we take only the part containing  $\frac{1}{4}$ , we have instead of the last two fractions other functions of  $(n'_1 + n'_2)$  and  $(n_1 + n_2)$ , viz.

$$\nu = R \left[ \frac{1}{(n'_1 + n'_2)^2} - \frac{1}{(n_1 + n_2)^2} + \frac{1}{4} \frac{a^2 E^2}{e^2} \left\{ \frac{1}{(n'_1 + n'_2)^4} - \frac{1}{(n_1 + n_2)^4} \right\} \right]. \quad (42)$$

This gives still no splitting of the lines. Since  $n'_1 + n'_2 < n_1 + n_2$ , the frequency  $\nu$  of the lines becomes only somewhat greater than according to Balmer's formula.

But we have still the second part of the second term of the series, leading to

$$\Delta\nu = Ra^2 \frac{E^2}{e^2} \left[ \frac{n'_1}{n'_2(n'_1 + n'_2)^4} - \frac{n_1}{n_2(n_1 + n_2)^4} \right], \quad . \quad . \quad (43)$$

and this gives a splitting of the lines; for the same value of  $n_1 + n_2$  can be obtained in a variety of ways, and similarly for  $n'_1 + n'_2$ .

Each spectrum line, such as  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , is characterized by given values of  $n_1 + n_2$  and  $n'_1 + n'_2$ . If, therefore, the value of  $n'_1 + n'_2$  can be made up in  $k'$  different ways so that  $\frac{n'_1}{n'_2(n'_1 + n'_2)^4}$  acquires  $k'$  different values, the first part of  $\Delta\nu$  will give rise to  $k'$  components. Similarly, if  $n_1 + n_2$  can be made up in  $k$  ways, the second part of  $\Delta\nu$  will give rise to  $k$  components. Thus, owing to both circumstances, we get in all  $kk'$  components. We may as well say that the first cause gives us  $k'$  component lines and that, due to the second cause, each of these is split into  $k$  lines, or *vice versa*.

Here the following considerations have to be taken into account.

1. The greater  $n_1 + n_2$ , the greater the number of ways in which this sum can be obtained, and thus the greater the number of components. At the same time, however,  $\frac{n_1}{n_2(n_1 + n_2)^4}$  becomes, in general, smaller; that is to say, the groups of components become more and more narrow.

2. The arithmetical possibilities can, of course, be limited in various ways. In the first place, the case  $n_2 = 0$ ,  $n'_2 = 0$  can be excluded, as it would give rise to a rectilinear orbit which would make the electron fly through the nucleus. Again, it can be assumed that in passing from one orbit to another the value of  $n_1$  does not increase (our  $n_1$  is Sommerfeld's  $n'$ ). Thus, lines for which  $n_1$  would increase will have the intensity zero. The number  $n_2$ , as it seems, may increase, but the corresponding lines are weak.

For the remaining lines Sommerfeld puts the intensity proportional to

$$\frac{n_2}{n_1 + n_2} \cdot \frac{n'_2}{n'_1 + n'_2}.$$

This provisional rule [now antiquated] would imply that circular orbits and passages from one circular orbit to another occur most often.

Let us first consider the Balmer series of hydrogen for which, to a first approximation,

$$\nu = R \left( \frac{1}{2^2} - \frac{1}{p^2} \right), \quad p = 3, \text{ etc.}$$

We have here

$$n'_1 + n'_2 = 2,$$

whence the following possibilities

$$n'_1 = 1, n'_2 = 1 \quad \text{and} \quad n'_1 = 0, n'_2 = 2.$$

The difference of the values of (43) for these two cases, which will be denoted by  $\Delta\nu_H$ , is

$$\Delta\nu_H = \frac{1}{16} R a^2,$$

since for hydrogen  $E = c$ . All lines should thus be doublets with the same frequency interval to which correspond, of course,



different wave-length intervals (for  $H_\alpha$  0.16 Å.U., for  $H_\beta$  0.07 Å.U., etc.).

That  $H_\alpha$  is a doublet, has already been shown, interferometrically, by Michelson and by Buisson and Fabry. Paschen, using a reflecting grating, saw  $H_\alpha$  as a double line in the second and third order.

Thus far the first term of (43). The second term of this expression gives rise to further complications.

For  $H_\alpha$ , for example,  $n_1 + n_2 = 3$ , so that we have three possible combinations,

$$\begin{aligned} n_1 &= 2, n_2 = 1 \\ n_1 &= 1, n_2 = 2 \\ n_1 &= 0, n_2 = 3. \end{aligned}$$

This gives a splitting of either of the two components of  $H_\alpha$  into a triplet.

Similarly, for  $H_\beta$  we have two quartets, and so on.

The distances between the components of the triplets and the quartets can all be expressed in terms of  $\Delta\nu_H$ .

If this resolution into triplets and quartets were accessible to observation, one could determine with precision the value of  $\Delta\nu_H$ .

Under the existing circumstances Paschen had to estimate it to a certain extent, using Sommerfeld's theory as a guide.

This theory, however, has received a stronger support from Paschen's observations on the spectrum of helium.

What used to be called the principal series of hydrogen has in reality to be ascribed to helium, namely to helium atoms which have lost one electron and are, therefore, positively charged [ionized]. In fact, we have to imagine the normal helium atom as consisting of a positive nucleus of charge  $2e$  and of two electrons revolving around it. If of these one only is left, we have a case to which the above theory can be applied, only that now  $E$  is twice and, therefore, the coefficient in (43) *four* times as great as for hydrogen, so that the separations will now be as many times greater. They can all be again expressed in terms of  $\Delta\nu_H$ .

If  $R$  be Rydberg's constant for hydrogen, the helium series alluded to is represented by

$$\nu = 4R \left( \frac{1}{3^2} - \frac{1}{p^2} \right).$$

As far as the first term is concerned the lines of this series are triplets and these are combined with quartets and more complex groups to which the second term gives rise. Paschen investigated these phenomena in detail. He has studied also the structure of the lines of the series

$$\nu = 4R \left( \frac{1}{4^2} - \frac{1}{p^2} \right)$$

and derived from the separation of the components of the lines of both series the value of  $\Delta\nu_H$ .

We have seen that Sommerfeld found for it (theoretically) the value  $\frac{1}{16} Ra^2$ , which turns out to be 0.363. According to Paschen's measurements  $\Delta\nu_H$  lies between 0.35 and 0.37.

Further details will be found in Sommerfeld's paper,\* p. 73.

So much concerning the term in Sommerfeld's formula which represents the splitting. Let us now consider the term giving small displacements of the lines.

Formula (42) can be written

$$\nu = R' \left[ \frac{1}{(n'_1 + n'_2)^2} - \frac{1}{(n_1 + n_2)^2} \right],$$

where

$$R' = 1 + \frac{1}{4} a^2 \frac{E^2}{e^2} \left[ \frac{1}{(n'_1 + n'_2)^2} + \frac{1}{(n_1 + n_2)^2} \right].$$

The different lines would thus give slightly different values for the Rydberg constant.

Let us compare, for example,  $H_\alpha$  and  $H_\beta$ . For both lines  $n'_1 + n'_2 = 2$ , while  $n_1 + n_2$  is 3 for the former, and 4 for the latter. Thus the difference of the  $R'$ -values is

$$\frac{1}{4} a^2 \left( \frac{1}{9} - \frac{1}{16} \right),$$

the  $R'$ -value derived from  $H_\alpha$  being greater than that derived from  $H_\beta$ . See the numerical results on p. 60 of Sommerfeld's paper.

## 9. RELATIVISTIC THEORY OF THE SPLITTING OF SPECTRUM LINES IN A MAGNETIC FIELD

We have thus far dealt with the derivation of the Balmer formula, the magnetic and the electric splitting and the fine

\* Cf. the literature at the end of this course of lectures.

structure of spectrum lines, that is to say, with the effects of a magnetic and an electric field and with the modifications introduced by the principle of relativity.

We should now be able to combine these different effects with each other. As an example of problems of this kind we will consider here the effect of a magnetic field taking, at the same time, into account the relativistic correction. In doing so, however, we will treat both the effect of the magnetic field and that correction as very small. The latter depends on  $v^2/c^2$ , and this will be considered as a very small quantity. Products of this quantity into others proportional to the magnetic field intensity will be neglected.

The equations of motion are (cf. p. 282)

$$\left. \begin{aligned} \dot{p}_x &= -q \frac{x}{r^3} - \frac{eH}{c} \dot{y}, \\ \dot{p}_y &= -q \frac{y}{r^3} + \frac{eH}{c} \dot{x}, \\ \dot{p}_z &= -q \frac{z}{r^3}, \end{aligned} \right\} \quad . \quad . \quad . \quad (44)$$

where

$$p_x = \frac{m\dot{x}}{\sqrt{1-v^2/c^2}}, \quad p_y = \frac{m\dot{y}}{\sqrt{1-v^2/c^2}}, \quad p_z = \frac{m\dot{z}}{\sqrt{1-v^2/c^2}}. \quad (45)$$

We pass again to spinning axes by the substitutions

$$\begin{aligned} x' &= x \cos \omega t + y \sin \omega t, \\ y' &= -x \sin \omega t + y \cos \omega t, \end{aligned} \quad \omega = \frac{eH}{2cm}.$$

From these we derive

$$\begin{aligned} \dot{x}' &= \dot{x} \cos \omega t + \dot{y} \sin \omega t - \omega x \sin \omega t + \omega y \cos \omega t, \\ \dot{y}' &= -\dot{x} \sin \omega t + \dot{y} \cos \omega t - \omega x \cos \omega t - \omega y \sin \omega t, \end{aligned}$$

whence, neglecting terms with  $\omega^2$ ,

$$\dot{x}'^2 + \dot{y}'^2 = \dot{x}^2 + \dot{y}^2 + 2\omega(\dot{x}y - \dot{y}x).$$

Thus, if  $v'$  be the velocity of the electron in the  $x', y', z$ -system, we can write (neglecting terms with  $\omega$  in expressions of the order  $v^2/c^2$ )

$$\sqrt{1 - \frac{v'^2}{c^2}} = \sqrt{1 - \frac{v^2}{c^2}}$$

and

$$\frac{m}{\sqrt{1 - v'^2/c^2}} = \frac{m}{\sqrt{1 - v^2/c^2}} = \mu, \text{ say.}$$

Further, let  $p'_x$ ,  $p'_y$  be the magnitudes which arise from (45) when  $\dot{x}$ ,  $\dot{y}$ ,  $v$  are replaced by  $\dot{x}'$ ,  $\dot{y}'$ ,  $v'$ . Then, by the last formula,

$$p'_x = \mu \dot{x}', \quad p'_y = \mu \dot{y}',$$

and

$$\begin{aligned} \dot{p}'_x &= \mu \ddot{x}' + \dot{\mu} \dot{x}' \\ &= \mu(\ddot{x} \cos \omega t + \ddot{y} \sin \omega t) + 2\omega m(-\dot{x} \sin \omega t + \dot{y} \cos \omega t) \\ &\quad + \dot{\mu}(\dot{x} \cos \omega t + \dot{y} \sin \omega t) \\ &= \dot{p}_x \cos \omega t + \dot{p}_y \sin \omega t + 2\omega m(-\dot{x} \sin \omega t + \dot{y} \cos \omega t). \end{aligned}$$

Substituting here the values (44) of  $\dot{p}_x$  and  $\dot{p}_y$  we find

$$\dot{p}'_x = -q \frac{x'}{r^3};$$

similarly,

$$\dot{p}'_y = -q \frac{y'}{r^3}, \quad \dot{p}'_z = -q \frac{z'}{r^3}.$$

These equations are of the same form as (44) for  $H=0$ . We can say, therefore, that in the presence of the magnetic field the motion with respect to the spinning axes is the same as in the absence of a field with respect to fixed axes. Thus it is enough so to determine the motion as if there were no field and then to give to the system a spin  $\omega$ .

As to the quantum conditions, we can retain those which were introduced in the absence of a magnetic field and which served to describe the motion of the electron in a given plane. These conditions remain satisfied when the system is given the said spinning motion, and we can now add the further condition that the moment of momentum resolved along the direction of the field shall be a multiple of  $h/2\pi$ . Since also the total moment of momentum is such a multiple, this amounts to requiring that the cosine of the angle between the spinning plane of the orbit and the plane perpendicular to the magnetic field shall have a rational value. As before (pp. 284, 286), we put for the said component of the moment of momentum  $p_3 \frac{h}{2\pi}$ .

Let now  $-A$  be the energy for one of the allowed motions when the spin is disregarded. What is its value in the actual motion, *i.e.* with the spin  $\omega$ ? We have derived it before by a geometrical reasoning. Now we can find it in the following way :

The potential energy is the same as without the spin. The kinetic energy is (p. 313)

$$mc^2 \left[ -1 + \frac{1}{\sqrt{1 - v^2/c^2}} \right] = \frac{1}{2}mv^2 \left( 1 + \frac{3}{4} \frac{v^2}{c^2} \right) \text{ in the system } x, y, z$$

and  $\frac{1}{2}mv'^2 \left( 1 + \frac{3}{4} \frac{v'^2}{c^2} \right) \text{ in the system } x', y', z.$

Since the first terms only have to be taken into account, the difference of the energies is

$$\frac{1}{2}m(v^2 - v'^2) = m\omega(yx - \dot{x}y) = p_3 \frac{h}{2\pi}.$$

As a matter of fact, the  $z$ -component of the moment of momentum is  $\mu\omega(yx - \dot{x}y)$ . But this can here be replaced by  $m\omega(yx - \dot{x}y)$ .

Thus, if the system passes suddenly from a state of motion characterized by  $A$  and  $p_3$  to another characterized by  $A'$  and  $p'_3$  (where  $-A$  and  $-A'$  are the energy values corresponding to the case  $H=0$ ), the frequency of the emitted radiation is

$$\nu = \frac{A' - A}{h} + \frac{1}{2\pi}(p_3 - p'_3).$$

The second term represents the Zeeman effect. It is clear that this will be exactly the same for all spectrum lines (and also for their fine-structure components). There can thus be no question of explaining in this manner the phenomenon observed by Paschen and Back, viz. the splitting, in a field of sufficient intensity, of a line which in the absence of a magnetic field is a fine doublet into a simple magnetic triplet.

## 10. EFFECT OF THE WOBBLING OF THE NUCLEUS

There is, in addition to those mentioned before, one more peculiarity of which Bohr's theory gives a striking explanation, viz. the effect of the wobbling of the nucleus upon the emitted spectrum. This was thus far disregarded, the nucleus, in view of its comparatively large mass, having been considered as fixed.

It appears, however, that the effect of its wobbling is just perceptible.

In treating this problem we may limit ourselves to circular motions. Let  $M$  be the mass of the nucleus,  $m$  that of the electron,

$r$  their mutual distance,  $q/r^2$  the attraction, and  $\dot{\phi}$  the angular velocity. Then

$$\frac{mM}{M+m} r \dot{\phi}^2 = \frac{q}{r^2}.$$

The kinetic energy of the system is

$$\frac{1}{2} \frac{mM}{M+m} r^2 \dot{\phi}^2,$$

hence, the component of momentum corresponding to  $\dot{\phi}$ ,

$$\frac{mM}{M+m} r^2 \dot{\phi}.$$

Of this the part  $M \left( \frac{m}{M+m} r \right)^2 \dot{\phi}$  belongs to  $M$ , and the remainder

$$m \left( \frac{M}{M+m} r \right)^2 \dot{\phi} \text{ to } m.$$

We introduce as quantum condition

$$\frac{mM}{M+m} r^2 \dot{\phi} = n \frac{h}{2\pi},$$

or, putting  $\frac{mM}{M+m} = \mu$ ,

$$\mu r^2 \dot{\phi} = n \frac{h}{2\pi}.$$

This, together with

$$\mu r \dot{\phi}^2 = \frac{q}{r^2},$$

gives

$$r = \frac{1}{\mu q} \frac{h^2}{4\pi^2} n^2.$$

The kinetic energy is

$$\frac{1}{2} \mu r^2 \dot{\phi}^2 = \frac{1}{2} \frac{q}{r},$$

and the potential energy,

$$-q/r,$$

so that, if  $-A$  be again the total energy,

$$A = \frac{1}{2} \frac{q}{r} = \frac{2\pi^2 \mu q^2}{h^2} \cdot \frac{1}{n^2}.$$

Let, as before,  $-e$  be the charge of the electron and  $E$  that of the nucleus. Then  $q = Ee$ , and

$$A = \frac{2\pi^2 \mu e^2 E^2}{h^2} \cdot \frac{1}{n^2}.$$



Thus the frequency of light emitted in passing from one state of motion to another will be

$$\nu = \frac{2\pi^2\mu e^2 E^2}{h^3} \left( \frac{1}{n'^2} - \frac{1}{n^2} \right).$$

Now,  $M$  is considerably greater than  $m$ , so that we can write

$$\mu = \frac{m}{1 + m/M} = m \left( 1 - \frac{m}{M} \right).$$

In the case of hydrogen  $m/M$  is about  $1/1850$ . Yet the accuracy of the wave-length measurements is so great, that even such a small fraction of the total amount can be discerned.

The effect of the term  $m/M$  can be tested by measuring it in a manner entirely independent of an accurate knowledge of the other magnitudes which come into play.

For this purpose it is enough to compare two well investigated spectra, viz. the Balmer series of hydrogen,  $H_\alpha$ ,  $H_\beta$ , etc., and the so-called principal series of hydrogen which actually belongs to helium [ionized helium, as before]. We will assume that the charge  $e$  and the mass  $m$  of the revolving electron are the same in both cases. Then for the hydrogen atom  $E=e$  and for the helium atom  $E=2e$ . The Rydberg constant for the hydrogen series is

$$\frac{2\pi^2\mu_H e^4}{h^3}, \text{ say } N_H,$$

and for the helium series,

$$\frac{8\pi^2\mu_{He} e^4}{h^3}, \text{ say } 4N_{He},$$

so that

$$N_{He} : N_H = \mu_{He} : \mu_H = \left( 1 - \frac{m}{M_{He}} \right) : \left( 1 - \frac{m}{M_H} \right).$$

Thus  $N_H$  must be somewhat smaller than  $N_{He}$ , viz.

$$\frac{N_H}{N_{He}} = \frac{1 - 1/1850}{1 - \frac{1}{4} \cdot 1/1850} = 1 - \frac{3}{4} \cdot \frac{1}{1850} = 1 - \frac{1}{2470}.$$

This is confirmed by Paschen's\* measurements, who has determined  $N_{He}$  and  $N_H$  with the greatest care.

\* Cf. the reference at the end of this course of lectures.

In fact, Paschen finds for the hydrogen line  $H_a$

$$\begin{array}{rcl}
 \lambda \text{ air (in } \text{\AA}.U.) & . & . & . & 6562.8451 \\
 \lambda \text{ air} \times (n_{76, 15} - 1) & . & . & . & 1.8141^* \\
 \lambda \text{ vacuum} & . & . & . & \hline
 & & & & 6564.6592 \\
 \nu = 1/\lambda_{vac.} & = & 15233.084 \\
 \nu : \left(\frac{1}{4} - \frac{1}{9}\right)^\dagger & = & 109678.205
 \end{array}$$

Relativity correction . . . 0.526

Result  $N_H = 109677.679$ .

From the measured wave-lengths of the first four hydrogen lines Paschen computes

|                          | $N_H$ .    | Weight. |
|--------------------------|------------|---------|
| $H_a$ . . . .            | 109677.679 | 6       |
| $H_\beta$ (Paschen) . .  | 109677.709 | 2       |
| $H_\beta$ (Meissner) . . | 109677.629 | 2       |
| $H_\gamma$ . . . .       | 109677.744 | 1       |
| $H_\delta$ . . . .       | 109677.793 | 1       |

Mean  $N_H = 109677.691 \pm 0.06$ .

For helium Paschen finds

$$N_{He} = 109722.144 \pm 0.04.$$

How closely the measured wave-lengths agree with this result appears from Paschen's numerous observations, *e.g.*, those on the group of lines in the helium spectrum for which (p. 321)  $p' = 3$ ,  $p = 7$ . Of this group, 2511, he has measured three components and found

|                       |          |          |          |
|-----------------------|----------|----------|----------|
| $\lambda$ air . . . . | 2511.249 | 2511.216 | 2511.117 |
| possible error .      | 0.004    | 0.004    | 0.002    |

On the other hand, Paschen's calculation, based on the value just found for  $N_{He}$ , is as follows :

\*  $n_{76, 15}$  is the refractive index of air at a pressure of 76 cm. and a temperature of  $15^\circ$ .

† The value given for  $\nu$  is the number of waves per centimetre, and  $\nu : (\frac{1}{4} - \frac{1}{9})$  is, apart from the relativistic correction (cf. end of Art. 8), the Rydberg constant corresponding to this "vibration number".

$$N_{He} = 109722.144$$

$$\text{Relativity correction } * \quad . \quad 0.766$$

$$4[(1/3)^2 - (1/7)^2] = 109722.910$$

$$\nu = 39808.7655$$

$$\lambda_{vac.} = 2512.0097$$

$$\lambda_{vac.} \times (n_{76, 15} - 1) = 0.7554$$

$$\lambda \text{ air} = 2511.2543.$$

From this value he finds, by Sommerfeld's theory, the wavelengths of the three components

$$2511.254 \qquad 2511.218 \qquad 2511.112,$$

which agree exceedingly well with the observed ones.

The difference between  $N_H$  and  $N_{He}$  is about 44.5, and this is the 2470th part of either, which is in very good agreement indeed with the result derived above from the mass ratio of the electron and the hydrogen nucleus. *Vice versa*, that ratio can be determined from the values found for  $N_H$  and  $N_{He}$ , and such a determination can undoubtedly be considered as the most accurate of all thus far known.

Taking 1.008 for the atomic weight of hydrogen and 3.99 for that of helium, Paschen finds

$$\frac{M_H}{m} = 1843.7.$$

Spectroscopic observations have thus proved that the nucleus moves indeed to an extent corresponding to the mass ratio.

## 11. THE RING-ELECTRON AND ITS DIFFICULTIES

It has once occurred to me that the absence of radiation as required for Bohr's model of the atom could perhaps be explained by supposing that what revolves around the nucleus is not a single electron † but a ring-shaped charge distributed continuously along the whole orbit; in other words, that the charge of

\* This is the correction mentioned at the end of Art. 8.

[† Of spherical or quasi-spherical shape, as usually imagined.]

the electron has distributed itself over such a ring. But if one imagines this, one encounters various difficulties.

1. In the formula for Rydberg's constant appears the mass of the electron. This is given the value derived from the electron theory,\* and then one gets the desired numerical agreement. Thus, if we wished to replace the electron moving in a circle by a rotating circular ring, we would have to ascribe to the latter a coefficient of self-induction corresponding to the mass of the electron which, with a properly chosen cross-section of the ring, could after all be accomplished.† Something similar could also be done with an elliptic ring which would replace an electron

[\* Including experiments on  $\beta$ -particles and kathode rays.]

† Let  $e$  be the charge of the ring per unit length,  $\omega$  the angular velocity,  $R$  the radius of the cross-section and  $a$  the radius of the ring;  $R \ll a$ . Then the intensity of the current will be

$$i = \omega a e$$

and the magnetic energy

$$T = \frac{1}{2} L i^2 = \frac{1}{2} L a^2 e^2 \omega^2.$$

Here

$$L = \frac{a}{c^2} \left( \log \frac{8a}{R} - \frac{7}{4} \right)$$

or, since  $R \ll a$ ,

$$L = \frac{a}{c^2} \log \frac{8a}{R},$$

so that we can write for the magnetic energy

$$\frac{a}{2c^2} e^2 a^2 \omega^2 \log \frac{8a}{R}.$$

We will compare this ring with a spherical electron of radius  $R'$ , moving in a circle of radius  $a$ , and require that the magnetic energy shall be the same in both cases. Let  $\omega'$  be the angular velocity of the electron and  $e'$  its charge. Since this is equal to the charge of the ring,

$$2\pi a e = e',$$

we have

$$\frac{a^3 e^2}{c^2} \omega^2 \log \frac{8a}{R} = \frac{e'^2}{6\pi R' c^2} a^2 \omega'^2;$$

from these two equations follows

$$\log \frac{8a}{R} = \frac{2\pi}{3} \frac{a}{R'} \frac{\omega'^2}{\omega^2}$$

and, if the angular velocities are assumed to be equal,

$$\log \frac{8a}{R} = \frac{2\pi}{3} \frac{a}{R'}.$$

The ring of electricity would thus have to be exceedingly thin. For, since  $a/R'$  is a great number,  $a/R$  must be still more so.

describing an elliptic orbit. This, however, would be too complicated and not very satisfactory.

2. Very much against the concept of such a ring are the results concerning the fine structure of spectrum lines. For this is explained by taking account of the changes as required by the theory of relativity, and one does not see how one could get something precisely equivalent in the case of a closed ring.

It has occurred to me that instead of a closed ring one could imagine a very great number of electrons distributed over the circle or the ellipse. Suppose that these particles are all equal and move along the orbit in precisely the same way, succeeding each other at any given point of the orbit in equal intervals of time. The radiation from such a system, though not exactly zero, is very weak, provided the number of particles  $N$  is great, say 10 or 100.

The total charge of these particles must be equal to  $-e$ , and thus, *e.g.* the charge of each equal to  $-e/N$ . If we still make their radii  $N$  times smaller than that of the original electron  $-e$ , then also their masses will be  $N$  times smaller. Thus the ratio of charge to mass, and therefore also the acceleration in a given field will for each of these small electrons be the same as for the large electron  $-e$ , and each of them taken by itself would move around the nucleus in exactly the same way as did the large electron. This holds even for the peculiarities of motion introduced by the relativity principle.

All the electrons could then revolve in this way simultaneously around the nucleus, were it not for their interaction. This, therefore, must be abolished in some way or other, *e.g.* by supposing that these small electrons exert upon each other forces of a non-electrical kind which just balance their repulsion, similarly as the mutual repulsion of the parts of a single electron is abolished by Poincaré's tensions.\* This would give a system

\* Let us consider an electron which in the state of rest is spherical, of radius  $R$ , with a uniform surface distribution of charge  $e$ , and which in translational motion with the velocity  $v$  becomes flattened to an ellipsoid, its original dimensions in the direction of motion being reduced in the ratio of 1 to  $(1 - v^2/c^2)^{\frac{1}{2}}$ . The corresponding electromagnetic momentum is found to be

$$G = \frac{e^2}{6\pi c^2 R} \frac{v}{(1 - v^2/c^2)^{\frac{1}{2}}},$$

and the electromagnetic energy,

$$\frac{e^2}{6\pi R} \left[ \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}} - \frac{1}{4} \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} \right].$$

which could serve to explain the spectroscopic effects under consideration and which, at the same time, would radiate as little as we please. In fact, the radiation from each particle

Both the momentum and the energy are mainly localised in the immediate neighbourhood of the electron.

In fact, the momentum can be written

$$\frac{v}{c^2} \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}} \int \left\{ \left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 \right\} dS,$$

where the integral [to be extended over the whole space] is to be taken for a spherical electron at rest,  $\phi$  being the electrostatic potential. The integral can be written  $\frac{2}{3} \int \left(\frac{d\phi}{dr}\right)^2 dS$ , and since  $\phi$  is of the form  $C/r$ , this becomes

$$\frac{8}{3} \pi C^2 \int \frac{dr}{r^2} = -\frac{8}{3} \pi C^2 \left| \frac{1}{r} \right|.$$

Whence we see that, *e.g.*, the space outside the sphere of radius  $10R$  contains only  $1/10$ , and that outside the sphere of radius  $100R$  only  $1/100$  of the total momentum. Something similar holds for the electromagnetic energy.

Herefrom we can conclude also that, if there are several electrons, to each of them can be attributed its own momentum and energy only when their mutual distances are great compared with their dimensions.

That the electromagnetic energy is not the whole energy of the electron can be seen as follows:

Put for brevity

$$m = \frac{e^2}{6\pi c^2 R}.$$

Then

$$G = \frac{mv}{\sqrt{1 - v^2/c^2}}.$$

If  $v$  varies slowly, the electron is acted upon by the force

$$\dot{G} = \frac{dG}{dv} \dot{v}.$$

The work done by this force per unit time will be equal to the rate of increase of the total energy  $E$ . Thus

$$\frac{dG}{dv} \dot{v} = \frac{dE}{dv} \dot{v}$$

or

$$\frac{dG}{dv} = \frac{dE}{dv}.$$

Now,

$$v \frac{dG}{dv} = \frac{mv}{(1 - v^2/c^2)^{\frac{3}{2}}},$$

and this is just the value we get for  $dE/dv$  if we take for  $E$  only the first term of the above given expression, viz.

$$\frac{e^2}{6\pi R} (1 - v^2/c^2)^{-\frac{1}{2}} = mc^2 (1 - v^2/c^2)^{-\frac{1}{2}}.$$

Thus there must still be a supplementary energy amounting to

$$\frac{e^2}{24\pi R} (1 - v^2/c^2)^{\frac{1}{2}} + C.$$

This is just the energy corresponding to Poincaré's tensions. In fact, Poincaré imagines the electron as a thin film with the charge  $e$ . If the electron



would be  $N^2$  times smaller than from the large electron  $-e$ , and the total effect would be still diminished by the mutual interference of the waves emitted by different particles.

All these ideas, however, must be given up in view of the wobbling of the nucleus as revealed by spectroscopic observations. For, if instead of a single electron there were a great number of revolving electrons, the nucleus would remain at rest. We must conclude, therefore, that in the hydrogen atom and the simply ionized helium atom ( $He^+$ ) there is indeed only one electron, such as it occurs in the cathode and  $\beta$ -rays, revolving around the nucleus.

Then, however, the difficulty of the absence of radiation persists, and one does not see at all how it could be removed. Owing to the motion of the electron around the nucleus the state at any fixed point of the aether will change continually (these changes manifest themselves, moreover, in the force exerted upon the nucleus, which determines its wobbling), and one does not understand why these changes should not propagate themselves outwards in the form of waves.

## 12. FURTHER DISCUSSION OF MOTIONS COMPATIBLE WITH THE QUANTUM CONDITIONS

Suppose we have integrated the equations of motion. This would give us a certain number of integration constants, viz.

is spherical, the electrical force just outside it is  $e/4\pi R^2$ , and to this corresponds the Maxwellian tension

$$T = \frac{e^2}{32\pi^2 R^4}.$$

To ensure equilibrium, this tension must be balanced by an equal tension on the inner side (or pressure on the outer side) of the film. Now, it can be shown that the same tension must exist when the electron moves and is, therefore, deformed in the way stated above. We can even say that, if there is such a constant tension, the electron, when set into motion, must necessarily be deformed.

But if there is a tension  $T$ , there will also be an energy

$$TV + C,$$

where  $V$  is the volume of the electron. Now,

$$V = \frac{4}{3}\pi R^3(1 - v^2/c^2)^{\frac{1}{2}},$$

so that

$$TV + C = \frac{e^2}{24\pi R}(1 - v^2/c^2)^{\frac{1}{2}} + C.$$

Notice that this supplementary energy (as well as Poincaré's tension) is *not* of electromagnetic nature.

six in the case of the motion of a single electron (and five only if we do not count the time constant  $t_0$ ). A quantum condition, in which some function of these integration constants is equated to a multiple of  $h/2\pi$ , limits to a certain extent the allowed motions. Let us fix our attention upon a given state of the electron; then, if we know also its velocity components, we can determine the values of the integration constants. The quantum condition gives us thus a relation between the admissible velocities at a point. It is clear that if the electron has, at a point  $P$ , one of these possible velocities, and if it then moves according to the equations of motion, it will have also in a subsequent point  $P'$  of its path a velocity which is there possible. ("Velocity" is to be taken with regard to both direction and size.)

Around the point  $P$  under consideration a velocity diagram can be constructed in which every velocity that the electron can have is represented by a point.

If  $n$  in  $n\hbar/2\pi$  is given a definite value, the quantum condition requires that the velocity-point should lie on a certain surface, and since  $n$  can be any integer, we get a set of such surfaces. We can say that the group of motions which are possible at  $P$  forms a simple discontinuous sequence (discontinuity in one direction). If there are two quantum conditions, we have two sets of surfaces, and the velocity-point must lie on their intersection lines. In this case we can speak of a twofold discontinuous sequence (continuity in one direction).

Finally, if there are three quantum conditions, we get three sets of surfaces. The possible velocity-points now form a kind of space lattice. They show a threefold discontinuity. If there were more than three quantum conditions, the co-ordinates could no longer be chosen arbitrarily. A point chosen at will could then, in general, not be reached by any possible motion. Only such points could be attained whose position satisfies one or more special conditions.

Keeping always to the same point  $P$ , we can consider also the energy corresponding to the possible motions. The discontinuity of the energy may, of course, be of a lower order than that of the possible motions themselves. Suppose, for instance, that there is a threefold discontinuity in the velocity-points, corresponding to the values of three numbers,  $n_1, n_2, n_3$ . It can then still happen that each time a set of points lie at an

equal distance from  $P$ , so that the energy corresponding to them is the same. For the potential energy is already determined by the position of  $P$  and the kinetic energy depends (also in relativistic mechanics) only on the size of the velocity. Through each of such sets of points a line can be drawn whose points are all equidistant from  $P$ .

In this case the energy would be doubly discontinuous. It would present a simple discontinuity if a set of the said lines lay on a spherical surface.

Let us now see what are, in the different cases treated above, the possible velocities at an arbitrarily chosen point  $P$ . For the sake of simplicity the nucleus will be supposed to remain at rest.

Let us first consider the case of an external electric field without the relativity correction (Epstein's theory).

We have had three quantum conditions (p. 302); namely, three expressions containing the three integration constants  $a$ ,  $A$ , and  $\beta$  were equated to  $n_1 h/\pi$ ,  $n_2 h/\pi$ , and  $n_3 h/\pi$ . The component of the moment of momentum along the  $x$ -axis (direction of electric force) was  $my^2\dot{\phi}$  (p. 294); this was equated to  $\sqrt{m} \cdot a$ . The total energy was  $-A$ , and its part representing the potential energy was written

$$-\frac{\kappa e^2}{r} + eEx.$$

Finally, as regards  $\beta$ , let us recall the formulae (p. 298)

$$m(\xi^2 + \eta^2)\dot{\xi} = \sqrt{mf_1(\xi)}$$

$$f_1(\xi) = -\frac{a^2}{\xi^2} - eE\xi^4 - 2A\xi^2 + 2e^2(\kappa + \beta);$$

$\xi$ ,  $\eta$  are co-ordinates which were introduced (p. 295) in the spinning meridian plane instead of  $x$  and  $y$  through the equations

$$\xi^2 = r + x, \quad \eta^2 = r - x.$$

Suppose the position co-ordinates and the velocity components of the electron are given. Then the constants  $A$ ,  $a$ ,  $\beta$  and therefore also the left-hand members of the quantum equations

$$F_1 = n_1 \frac{h}{\pi}, \quad F_2 = n_2 \frac{h}{\pi}, \quad F_3 = n_3 \frac{h}{\pi}$$

can be calculated. The latter can thus be considered as functions of the co-ordinates and the velocity components, and the quantum

conditions as relations between these six quantities. But since these conditions are only three in number, we can, *e.g.*, choose arbitrarily the velocity components; then the conditions will determine the places where these velocities can occur. Or, what seems more natural, we can choose the place at our pleasure; then the conditions will determine, in size and direction, the velocity with which the electron can move at that place. If now the electron has at a point  $P$  such a "permitted" velocity and if it moves according to the laws of mechanics, it will have also at each successive point of the path a velocity which is there permitted.

In the second place we will consider the case of no external field. We then arrive at different results according as we start from Sommerfeld's quantum conditions for the field-free case or from Epstein's conditions for the limiting case  $E=0$ .

If we first take a plane passing through the centre  $O$  and apply Sommerfeld's quantum conditions, we have for that plane two equations of the form

$$F_1 = n_1 \frac{h}{\pi}, \quad F_2 = n_2 \frac{h}{\pi}.$$

Thus the velocities which are possible at a point will be discontinuous in two directions. But the plane in question can be turned about the line joining the nucleus with the considered point, retaining always the same discontinuous distribution of possible velocities. Every possible velocity-point will then describe a circle. Thus the possible velocity-points will be distributed in space upon a double system of circles.

On the other hand, the possible velocities can be determined by starting from Epstein's conditions and putting therein  $E=0$ . The distribution of the possible velocity-points is then continuous in two directions, so that there remains only a discontinuity in one direction. To see this we note that, if  $x$  and  $y$  be the co-ordinates in the rotating meridian plane, the rectangular space co-ordinates are

$$x, \quad y \cos \phi, \quad y \sin \phi,$$

and, therefore, the velocity components,

$$\dot{x}, \quad \dot{y} \cos \phi - y \dot{\phi} \sin \phi, \quad \dot{y} \sin \phi + y \dot{\phi} \cos \phi.$$

These give for the moment of momentum  $M$  with respect to  $O$ , per unit mass,

$$M^2 = (x\dot{y} - y\dot{x})^2 + r^2 y^2 \dot{\phi}^2$$

or, in terms of the co-ordinates  $\xi$  and  $\eta$ ,

$$M^2 = \frac{1}{4}(\xi^2 + \eta^2)(\xi\dot{\eta} - \eta\dot{\xi})^2 + \frac{r^2}{m\xi^2\eta^2}\alpha^2,$$

where we have already introduced one of the integration constants,  $\alpha$ .

Now, as we have found before (p. 298),

$$(\xi^2 + \eta^2)\dot{\xi} = \sqrt{\frac{1}{m}f_1(\xi)}, \quad (\xi^2 + \eta^2)\dot{\eta} = \sqrt{\frac{1}{m}f_2(\eta)}.$$

Thus

$$M^2 = \frac{1}{4} \left[ \xi \sqrt{\frac{1}{m}f_2(\eta)} - \eta \sqrt{\frac{1}{m}f_1(\xi)} \right]^2 + \frac{r^2}{m\xi^2\eta^2}\alpha^2,$$

where, if we put  $E=0$ ,

$$f_1(\xi) = -\frac{\alpha^2}{\xi^2} - 2A\xi^2 + 2e^2(\kappa + \beta)$$

$$f_2(\eta) = -\frac{\alpha^2}{\eta^2} - 2A\eta^2 + 2e^2(\kappa - \beta).$$

Ultimately, therefore, the quantum conditions for  $E=0$  become (cf. pp. 306-307)

$$\begin{aligned} \sqrt{\frac{1}{2}mA} \left\{ \frac{e^2}{A}(\kappa + \beta) - \alpha \sqrt{\frac{2}{A}} \right\} &= n_1 \frac{h}{\pi} \\ \sqrt{\frac{1}{2}mA} \left\{ \frac{e^2}{A}(\kappa - \beta) - \alpha \sqrt{\frac{2}{A}} \right\} &= n_2 \frac{h}{\pi} \\ 2\sqrt{ma} &= n_3 \frac{h}{\pi}. \end{aligned}$$

If  $n_1$ ,  $n_2$ ,  $n_3$  are given any chosen integer values, these conditions will determine the integration constants  $\alpha$ ,  $\beta$ , and  $A$ . Thus also the energy and the size of the velocity at a given point will be known. Since, however,  $E$  is nil, the  $x$ -axis can be drawn through  $O$  in any direction whatever; in other words, the angle  $\theta$  between  $OP$  and that axis can be chosen arbitrarily. But, whatever this angle, our formulae in which  $\alpha$ ,  $A$ , and  $\beta$  have the values corresponding to the chosen  $n_1$ ,  $n_2$ ,  $n_3$  will always represent a possible motion. Now,

$$\xi^2 = r + x = 2r \cos^2 \frac{\theta}{2}, \quad \eta^2 = r - x = 2r \sin^2 \frac{\theta}{2},$$

and when these values are substituted in  $f_1(\xi)$  and  $f_2(\eta)$  appearing in the moment  $M$ , the latter will contain also the angle  $\theta$ . Since



this angle is liable of a continuous variation, the same will be the case of  $M$ .

Thus a possible velocity at a fixed point of space  $P$  can, without ceasing to be possible, be varied continuously in such a way that, while its size remains constant, its moment with respect to  $O$  varies. But this is possible only if the angle between the velocity and  $OP$  varies. Thus we get a continuum of velocity-points, all equidistant from  $P$ . The locus of these points does not coincide with a circle having  $OP$  for its axis, so that rotating the diagram about  $OP$  we get as velocity-points all the points upon a certain sphere. Ultimately, therefore, we have a discontinuous series of such spheres corresponding to the values which the energy assumes for different sets of  $n_1, n_2, n_3$ .

Notice that, whether we follow Sommerfeld's method or take the limiting case of Epstein's conditions, we always find the same possible values for the energy. This means that the circles around the line  $OP$ , which are obtained by the former method, lie all upon the spheres yielded by the latter method.

There is thus, so far as the energy is concerned, no disagreement between the two conclusions arrived at, and they do not clash with each other with respect to the possible velocities if we so view the position that one method does indeed give us a number of possible velocity-points but without asserting the impossibility of all others.

It seems, however, that one would come to a discrepancy if one applied the corresponding considerations taking account of the relativity terms. In fact, a theory such as Epstein's leads, also with the inclusion of such terms, to definite possible motions. Having determined these we could again pass to the case  $E=0$ . Suppose that we then find  $PA$  as representing a possible velocity at the point  $P$ . The formulae which give us this can again be applied with different values of the angle  $\theta$ , this angle being continuously varied.

When we did so without taking account of the relativistic terms,  $PA$  changed continually, making each time another angle with  $OP$ , and it cannot be supposed that now [with these terms]  $PA$  will retain the same direction or make with  $OP$  permanently the same angle. The point  $A$  will thus describe a line which does not coincide with an arc of a circle with  $OP$  as axis. Now, when the diagram is rotated about  $OP$ , this line gives a certain surface,



and one gets ultimately a simple discontinuity of possible motions [velocities], whereas for the explanation of the fine structure of the spectrum lines a double discontinuity is required, as it occurs in Sommerfeld's theory.

### 13. THE MOTION OF AN ELECTRON IN THE FIELD OF TWO CENTRES

We can imagine that in the case treated by Epstein there is, besides the nucleus, another charged point fixed at an infinite distance. Now, it is worth while to notice that one can treat with equal ease the more general case of any two fixed centres  $A_1, A_2$ . The complete formulae for this case can be found in Jacobi's "Vorlesungen über Dynamik". They are still somewhat simplified if instead of the distances  $r_1$  and  $r_2$  of the electron  $P$  from the centres  $A_1$  and  $A_2$  the two co-ordinates

$$u = \frac{1}{2}(r_1 + r_2), \quad v = \frac{1}{2}(r_1 - r_2)$$

are introduced, the third co-ordinate being again the angle  $\phi$  which the plane  $A_1A_2P$  makes with a fixed plane through  $A_1A_2$ .

Let  $A_1A_2 = 2f$ .

Then the kinetic energy is

$$T = \frac{1}{2}m \left\{ \frac{u^2 - v^2}{u^2 - f^2} \dot{u}^2 + \frac{u^2 - v^2}{f^2 - v^2} \dot{v}^2 + \frac{(u^2 - f^2)(f^2 - v^2)}{f^2} \dot{\phi}^2 \right\}$$

or, if  $p_u, p_v, p_\phi$  are the momenta corresponding to the three co-ordinates,

$$T = \frac{1}{2m} \left\{ u^2 - f^2 p_u^2 + \frac{f^2 - v^2}{u^2 - v^2} p_v^2 + \frac{f^2}{(u^2 - f^2)(f^2 - v^2)} p_\phi^2 \right\}.$$

The potential energy being

$$U = -\frac{k_1}{r_1} - \frac{k_2}{r_2} = -\frac{k_1}{u+v} - \frac{k_2}{u-v},$$

the equation  $T + U = -A$ , with  $p_u, p_v, p_\phi$  replaced by  $\partial W / \partial u, \partial W / \partial v, \partial W / \partial \phi$  will give us the partial differential equation upon which the problem depends. After multiplication by  $2m(u^2 - v^2)$  this equation assumes the form

$$(u^2 - f^2) \left( \frac{\partial W}{\partial u} \right)^2 + (f^2 - v^2) \left( \frac{\partial W}{\partial v} \right)^2 + \left( \frac{f^2}{u^2 - f^2} + \frac{f^2}{f^2 - v^2} \right) \left( \frac{\partial W}{\partial \phi} \right)^2 - 2m[k_1(u-v) + k_2(u+v) - A(u^2 - v^2)] = 0.$$

Now,  $W$  can be split into three parts depending on  $u$ ,  $v$ ,  $\phi$  respectively, and since  $p_\phi$  is constant, say  $p_\phi = a$ , we can take for the third part  $a\phi$ . Thus we have

$$W = W_1(u) + W_2(v) + a\phi$$

with the two equations :

$$(u^2 - f^2) \left( \frac{dW_1}{du} \right)^2 + \frac{a^2 f^2}{u^2 - f^2} - 2m(k_1 + k_2)u + 2mAu^2 + \beta = 0,$$

$$(f^2 - v^2) \left( \frac{dW_2}{dv} \right)^2 + \frac{a^2 f^2}{f^2 - v^2} + 2m(k_1 - k_2)v - 2MAv^2 - \beta = 0,$$

where  $\beta$  is a new constant.

From these equations we can derive

$$\frac{dW_1}{du} = \sqrt{f_1(u)}, \quad \frac{dW_2}{dv} = \sqrt{f_2(v)},$$

where  $f_1(u)$  and  $f_2(v)$  are rather complicated functions of their arguments, leading to elliptic integrals.

Without entering into details we will note only that if the electron is not to escape into infinity, there must exist extreme values  $u_1$ ,  $u_2$  for  $u$ , and similarly for  $v$ . The function  $f_1(u)$  vanishes for  $u = u_1$  and  $u = u_2$  and is positive between these limits, and the first quantum condition becomes

$$2 \int_{u_1}^{u_2} \sqrt{f_1(u)} du = n_1 h ;$$

similarly, the second condition,

$$2 \int_{v_1}^{v_2} \sqrt{f_2(v)} dv = n_2 h,$$

while the third condition is

$$2\pi a = n_3 h.$$

These quantum conditions determine the three integration constants  $A$ ,  $a$ ,  $\beta$ . We get again, for every position of the electron, a manifold of possible velocity-points which is discontinuous in three directions.

#### 14. EFFECT OF THE WOBBLING OF THE NUCLEUS IN THE CASE OF AN EXTERNAL ELECTRIC FIELD

We have already investigated the effect of the wobbling of the nucleus under simple assumptions. Let us now see how this

effect can be taken into account in the more complicated cases which we have treated. In the first place we will consider the case of an external electric field.

Let  $-e$  be again the charge of the electron,  $\kappa e$  that of the nucleus, and  $E$  the electric force coinciding in direction with the  $x$ -axis. Further, let  $m$  and  $M$  be the masses,  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$  the co-ordinates of the electron and the nucleus respectively, and  $r$  their mutual distance. Then the equations of motion are

$$\begin{aligned} m\ddot{x}_1 &= \kappa e^2 \frac{x_2 - x_1}{r^3} - eE & M\ddot{x}_2 &= \kappa e^2 \frac{x_1 - x_2}{r^3} + \kappa eE \\ m\ddot{y}_1 &= \kappa e^2 \frac{y_2 - y_1}{r^3} & M\ddot{y}_2 &= \kappa e^2 \frac{y_1 - y_2}{r^3} \\ m\ddot{z}_1 &= \kappa e^2 \frac{z_2 - z_1}{r^3} & M\ddot{z}_2 &= \kappa e^2 \frac{z_1 - z_2}{r^3}. \end{aligned}$$

If  $x_0, y_0, z_0$  be the co-ordinates of the centre of gravity, then

$$(m + M)\ddot{x}_0 = (\kappa - 1)eE, \quad \ddot{y}_0 = 0, \quad \ddot{z}_0 = 0.$$

Put  $x = x_1 - x_0, y = y_1 - y_0, z = z_1 - z_0$  and denote by  $\rho$  the distance of the electron from the centre of gravity. Then

$$\begin{aligned} x_2 - x_1 &= \left(1 + \frac{m}{M}\right)(x_0 - x_1) = -\left(1 + \frac{m}{M}\right)x. \\ r &= \left(1 + \frac{m}{M}\right)\rho, \end{aligned}$$

and therefore,

$$\begin{aligned} \ddot{x} &= -\frac{\kappa e^2}{m} \left(\frac{M}{M+m}\right)^2 \frac{x}{\rho^3} - \left(\frac{1}{m} + \frac{\kappa - 1}{m + M}\right)eE \\ \ddot{y} &= -\frac{\kappa e^2}{m} \left(\frac{M}{M+m}\right)^2 \frac{y}{\rho^3} \\ \ddot{z} &= -\frac{\kappa e^2}{m} \left(\frac{M}{M+m}\right)^2 \frac{z}{\rho^3}. \end{aligned}$$

These equations are exactly of the same form as those which hold for a fixed nucleus. Thus the corresponding quantum conditions can be set up without trouble.

## 15. EFFECT OF THE WOBBLING OF THE NUCLEUS IN THE THEORY OF THE FINE STRUCTURE

In this theory the wobbling of the nucleus cannot be taken into account with perfect rigour. For since the velocities of the

nucleus and the electron are very different from each other and (as a rule) variable, there can, strictly, be no longer the question of a constant ratio of their momenta.\* But we can proceed approximately as follows.

The momentum of the electron has the components

$$\frac{m(\dot{x}_1, \dot{y}_1, \dot{z}_1)}{\sqrt{1 - v_1^2/c^2}},$$

and that of the nucleus,

$$\frac{M(\dot{x}_2, \dot{y}_2, \dot{z}_2)}{\sqrt{1 - v_2^2/c^2}},$$

for which we can write, approximately,

$$m\left(1 + \frac{v_1^2}{2c^2}\right)(\dot{x}_1, \dot{y}_1, \dot{z}_1)$$

and

$$M\left(1 + \frac{v_2^2}{2c^2}\right)(\dot{x}_2, \dot{y}_2, \dot{z}_2).$$

Thus the equations of motion (of which it will be enough to write down those for the  $x$ -axis) become

$$m\ddot{x}_1 = \frac{\kappa e^2}{r^3}(x_2 - x_1) - m \frac{d}{dt} \left( \frac{\dot{x}_1 v_1^2}{2c^2} \right),$$

$$M\ddot{x}_2 = \frac{\kappa e^2}{r^3}(x_1 - x_2) - M \frac{d}{dt} \left( \frac{\dot{x}_2 v_2^2}{2c^2} \right).$$

These give for the centre of gravity  $x_0, y_0, z_0$ , defined in the usual way,

$$(m + M)\ddot{x}_0 = -\frac{d}{dt} \left\{ \frac{m\dot{x}_1 v_1^2 + M\dot{x}_2 v_2^2}{2c^2} \right\}$$

$$m\ddot{x}_0 = -\frac{m}{m + M} \frac{d}{dt} \left\{ \frac{m\dot{x}_1 v_1^2 + M\dot{x}_2 v_2^2}{2c^2} \right\}$$

or, if  $x, y, z$  are again the co-ordinates of the electron with respect to the centre of gravity,

$$m\ddot{x} = m(\ddot{x}_1 - \ddot{x}_0)$$

$$= \frac{\kappa e^2}{r^3}(x_2 - x_1) - \frac{m}{m + M} \frac{d}{dt} \left\{ \frac{(m + M)\dot{x}_1 v_1^2 - m\dot{x}_1 v_1^2 - M\dot{x}_2 v_2^2}{2c^2} \right\}$$

$$= \frac{\kappa e^2}{r^3}(x_2 - x_1) - \frac{mM}{m + M} \frac{d}{dt} \left\{ \frac{\dot{x}_1 v_1^2 - \dot{x}_2 v_2^2}{2c^2} \right\}.$$

---

[\* In fine, the relativistic problem of two bodies has not been rigorously solved.]

Now,  $\dot{x}_2 v_2^2$  can be neglected in presence of  $\dot{x}_1 v_1^2$  and the factor  $mM/(m+M)$  can be replaced by  $m$ . Again, the factor  $\dot{x}_1$  in  $\dot{x}_1 v_1^2$  can be replaced by  $\dot{x}$  and  $v_1^2$  by  $v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$ . Thus,

$$m\ddot{x} = \frac{\kappa e^2}{r^3}(x_2 - x_1) - m \frac{d}{dt} \left\{ \frac{\dot{x} v^2}{2c^2} \right\},$$

with two similar equations for  $y$  and  $z$ .

Now, the attractive force appearing in these equations can be expressed in terms of the co-ordinates  $x, y, z$  and the distance of the electron from the centre of gravity of the system\* considered as due to a certain electric charge placed at the centre of gravity.

Thus we see that the motion of the electron with respect to the centre of gravity of the system is governed by equations of the same form as for a fixed nucleus, so that there is no difficulty in applying the quantum hypothesis.

## 16. RELATIVISTIC THEORY OF THE STARK EFFECT

To close these remarks on the quantum theory of the spectrum lines we will still point out the difficulties which one encounters when one tries to treat the motion under the influence of an external electric field  $E$  taking account of relativistic mechanics. We have had (p. 314) the partial differential equation

$$mc^2 \sqrt{1 + \frac{Q}{m^2 c^2}} - mc^2 + U = -A, \quad . \quad . \quad (46)$$

where  $U$  was the potential energy, the constant  $-A$  the total energy, and

$$Q = \left( \frac{\partial W}{\partial x} \right)^2 + \left( \frac{\partial W}{\partial y} \right)^2 + \left( \frac{\partial W}{\partial z} \right)^2.$$

If we introduce here the co-ordinates  $x, y$ , and  $\phi$  (denoting now

$$[* \text{ In fact, } x = x_1 - x_0 = x_1 - \frac{mx_1 + Mx_2}{m+M} = \frac{M}{m+M}(x_1 - x_2),$$

$$\text{so that } x_1 - x_2 = \left( 1 + \frac{m}{M} \right) x, \text{ etc.,}$$

$$\text{and } r^2 = \left( 1 + \frac{m}{M} \right)^2 (x^2 + y^2 + z^2).]$$

by  $x, y$  the co-ordinates in the meridian plane, cf. p. 294), so that the rectangular co-ordinates become

$$x, \quad y \cos \phi, \quad y \sin \phi,$$

then

$$Q = \left( \frac{\partial W}{\partial x} \right)^2 + \left( \frac{\partial W}{\partial y} \right)^2 + \frac{1}{y^2} \left( \frac{\partial W}{\partial \phi} \right)^2,$$

and finally, replacing  $x$  and  $y$  by the co-ordinates  $\xi$  and  $\eta$ , which were introduced through  $\xi^2 = r + x$ ,  $\eta^2 = r - x$ ,

$$Q = \frac{1}{(\xi^2 + \eta^2)} \left[ \left( \frac{\partial W}{\partial \xi} \right)^2 + \left( \frac{\partial W}{\partial \eta} \right)^2 \right] + \frac{1}{\xi^2 \eta^2} \left( \frac{\partial W}{\partial \phi} \right)^2. \quad (47)$$

The potential energy is

$$U = -\frac{2\kappa e^2}{\xi^2 + \eta^2} + \frac{1}{2}eE(\xi^2 - \eta^2). \quad (48)$$

In order to see whether the variables can be separated we have to solve (46) for  $Q$ . This gives

$$c^2 Q = -2Amc^2 + A^2 - 2(mc^2 - A)U + U^2. \quad (49)$$

Substitute here the value (47), remembering that, by (11),  $\partial W / \partial \phi = a$  (constant), and multiply by  $(\xi^2 + \eta^2)$ . Then the last term of the left-hand member of (49) will become

$$\left( \frac{1}{\xi^2} + \frac{1}{\eta^2} \right) c^2 a^2.$$

The right-hand member of (49) will consist of three groups of terms.

We have, first of all, the terms independent of  $U$ . These contain the factor  $(\xi^2 + \eta^2)$ .

Next, the term with  $U$ , after the multiplication by  $(\xi^2 + \eta^2)$ , consists of terms with  $(\xi^4 - \eta^4)$  and terms without  $\xi$  or  $\eta$ . Thus, so far as these terms are concerned, the variables can be separated.

Finally, in  $U^2$  occur terms with

$$\frac{1}{(\xi^2 + \eta^2)^2}, \quad \frac{\xi^2 - \eta^2}{\xi^2 + \eta^2}, \quad \text{and} \quad (\xi^2 - \eta^2)^2,$$

of which, however, the last can be omitted since it contains also  $E^2$ . The term with  $\frac{\xi^2 - \eta^2}{\xi^2 + \eta^2}$  offers, as to the separation of the variables, no difficulty. Such, however, is the case of the term



with  $\frac{1}{(\xi^2 + \eta^2)^2}$ . For, after the multiplication by  $(\xi^2 + \eta^2)$ , this gives  $\frac{1}{\xi^2 + \eta^2}$ , so that the variables are not separated.

## 17. SOMMERFELD'S THEORY OF ROENTGEN RAYS

Sommerfeld has given also a very remarkable application of Bohr's theory to Roentgen rays. He was preceded in this field by others (Moseley, Rydberg), but he has been the first to work out the theory.

His theory follows closely that of the optical spectrum series. There are, however, some points in which they differ.

In the first place, we have here to do with radiations which are emitted by elements of high atomic weight. The atomic number, also, as introduced by van den Broek and before him by Rydberg, is high. In Moseley's measurements it ranges from 13 (Al) to 79 (Au).

We can now say with certainty that the atomic number represents the positive charge of the nucleus [in electron units]. Thus, if this number be denoted, after Sommerfeld, by  $Z$ , we have  $Z$  negative electrons revolving around the nucleus, and it is clear that there can be no question of a rigorous solution of the equations of motion. This could be obtained only for special cases, as *e.g.* that of a number of electrons spaced in equal distances on a circle and revolving on it with equal velocity (such as the two electrons in the model proposed for the hydrogen molecule). But an exact treatment of more complicated motions, in anything like ellipses, say, is out of the question.

Yet the formulae which were found for the hydrogen and the [ionized] helium spectrum can be applied to the Roentgen spectra, though only with a certain modification, wherewith the theory assumes a semi-empirical character.

The modification alluded to is that we deal with the atomic system as if the charge of the nucleus were not  $Z$  but somewhat smaller, say  $Z-p$ . To a certain extent this can be accounted for by imagining that some of the  $Z$  electrons are placed more closely to the nucleus than that whose motion is being investigated. If the remaining electrons, which lie farther out, were uniformly distributed over a sphere, they would have on the whole no

influence, and one could then get a rough approximation by assuming that the nucleus charge is smaller than  $Z$  by an amount of the order of magnitude of the total charge of the inner electrons. If all the inner electrons were placed *in* the nucleus itself, then of course  $Z$  would have to be diminished by the exact number of these electrons.

That this defectively supported procedure has rendered (as will be seen presently) such good services, is rather surprising. But it must be kept in mind that the number  $p$ , to be subtracted from  $Z$ , is in most cases small, so that its effect is not great.

It is, further, of importance that the fine structure which is accounted for by relativistic mechanics plays in the case of Roentgen spectra such a prominent rôle.

In so far as the present investigation is connected with that of Art. 8, we will use here Sommerfeld's notation. Notice, therefore, that in Art. 8,  $n_1$ ,  $n_2$ ,  $a$  were written for Sommerfeld's symbols  $n'$ ,  $n$ ,  $a$  which henceforth will be used.

As we saw before, Sommerfeld found for the energy of an allowed motion

$$W = -\frac{Nh}{(n+n')^2} \left(\frac{E}{e}\right)^2 \left[ 1 + \frac{\alpha^2}{(n+n')^2} \left(\frac{E}{e}\right)^2 \left\{ \frac{1}{2} + \frac{n'}{n} \right\} \right], \quad (50)$$

where  $N$  is Rydberg's constant (fixed nucleus, hydrogen atom) and  $E$  the charge of the nucleus, while

$$\alpha = \frac{2\pi e^2}{hc} = 7 \cdot 10^{-3},$$

$$\alpha^2 = 5 \cdot 30 \cdot 10^{-5},$$

a universal constant.

$n$  and  $n'$  are whole numbers appearing in the quantum conditions. If the relativistic terms are entirely disregarded, we have only  $(n+n')^2$  in the denominator, and this has for any given term of the Balmer formula a determined value. And although the corresponding value of  $(n+n')$  can still be made up of integers in a variety of ways, this would have no influence upon the energy  $W$  of the motion in question. If, however, the relativity terms are taken into account, the different values which, for a fixed  $(n+n')$ , can be assigned to  $n$  and  $n'$  will give slightly different values for  $W$ . Whence the splitting in the fine structure, as described before.

Let us recall, in particular, that the value  $n+n'=1$  can be

obtained only in one way, viz. by  $n=1$ ,  $n'=0$ , since  $n=0$ ,  $n'=1$  would correspond to a rectilinear orbit which was excluded. For  $n+n'=2$ , however, we have two possibilities,  $n=2$ ,  $n'=0$  and  $n=1$ ,  $n'=1$ .

Since the splitting in the fine structure is proportional to  $(E/e)^4$ , it was for helium lines 16 times as great as for hydrogen lines. Still much more is it increased in the case of Roentgen rays, being proportional to  $(Z-p)^4$ . Thus it comes that the splitting plays here a prominent rôle in spite of the fact that the determination of the wave-lengths is so much less accurate. It gives rise to doublets which, compared with the fine structure of helium lines, have an enormous separation of the components.

The relativistic terms attain for the Roentgen rays such high values that the formula (50) can no longer be considered as sufficiently accurate. It will be remembered that this formula was arrived at by developing the energy into a series of ascending powers of  $\alpha^2 = 5.3 \cdot 10^{-5}$  and retaining only the terms in  $\alpha^2$  and  $\alpha^4$ . Sommerfeld has, therefore, extended the series development, including the terms in  $\alpha^6$  and  $\alpha^8$ . (This series development was given in Art. 8, p. 318.) When the higher terms are taken into account, the agreement with the experimental data becomes indeed distinctly better, which again speaks for the intrinsic value of the theory.

That the relativistic terms become for Roentgen rays so prominent is, of course, due to the high velocities which can be attained by the electrons. And that this is a necessary consequence of the great nucleus charge, can best be seen on the example of circular motion.\*

Another point of great importance, and one which has simplified the building up of the theory, is that the Roentgen spectra are, much more nearly than the optical ones, of the same kind for all elements. So much so, in fact, that one finds in all spectra the same lines or the same series of lines (although there are now and then gaps in the observations).

\* In fact, the radius of a circular orbit being  $r = \frac{1}{mq} \frac{h^2}{4\pi^2}$ , we have  $\frac{q}{mr} = \frac{4\pi^2 q^2}{h^2}$ , whence the velocity

$$v = \sqrt{\frac{q}{mr}} = \frac{2\pi q}{h} = \frac{2\pi eE}{h} = \frac{2\pi Ze^2}{h} = \frac{6.28 \cdot 22.8 \cdot 10^{-20}}{6.4 \cdot 10^{-27}} = Z \cdot 20 \cdot 10^7 \text{ Z.}$$

Thus, e.g. for  $Z=90$ ,  $v = 1800 \cdot 10^7 = 1.8 \cdot 10^{10}$  cm/sec.

Accordingly, when we speak of a certain line, we can have in mind all the corresponding lines, one for each element, and all of them can be denoted by the same symbol. The wave numbers ( $\nu$ ) of these lines will be given, as functions of  $Z$ , by one and the same formula.

As in the simple case of the Balmer series of hydrogen we have here a number of possible states of motion (to be distinguished by 1, 2, 3, . . .). Each of these can again be characterised by the energy (say,  $-A_1$  and  $-A_2$ ), and we have for the wave-number of the radiation emitted in passing from the state 2 to the state 1

$$\nu = \frac{1}{h}(A_1 - A_2) = \frac{A_1}{h} - \frac{A_2}{h}.$$

This can also be interpreted by stating that  $A_1/h$  is the wave-number which would be emitted if the electron passed from an infinite distance to the state 1; similarly for  $A_2/h$ . Thus we come to associate with each state of motion a definite wave-number. The wave-numbers of the emitted rays are then expressed by the difference of two such characteristic wave-numbers [or "terms"].

Sommerfeld denotes the different states of motion by  $K, L, M, N, O$ , etc., and uses these letters also for the associated characteristic wave-numbers. He denotes the corresponding values of  $p$  by  $k, l$ , etc.

We give here Sommerfeld's results for the first two characteristic wave-numbers.

The first of these is

$$K = N^* \frac{(Z-k)^2}{a^2} \left[ 1 + \frac{\alpha^2}{4} \frac{(Z-k)^2}{a^2} + \frac{\alpha^4}{8} \frac{(Z-k)^4}{a^4} + \frac{5\alpha^6}{64} \frac{(Z-k)^6}{a^6} \right],$$

where  $a$  will turn out to be equal to 1. It is with a view to this value that the coefficients  $\frac{1}{4}, \frac{1}{8}, \frac{5}{64}$  have been obtained. In connection with this there is only *one* wave-number  $K$ .

There are two wave-numbers  $L$ , to be distinguished as  $L$  and  $L'$ , viz.

$$L = N^* \frac{(Z-l)^2}{b^2} \left[ 1 + \frac{\alpha^2}{4} \frac{(Z-l)^2}{b^2} + \frac{\alpha^4}{8} \frac{(Z-l)^4}{b^4} + \frac{5\alpha^6}{64} \frac{(Z-l)^6}{b^6} \right]$$

\* In this and the following formulae the factor  $N$  is not a characteristic wave-number but Rydberg's constant. In the sequel  $N$  is used also for a characteristic wave-number [ $N$ -term], but this will scarcely give rise to a misunderstanding.

and

$$L' = N \frac{(Z-l)^2}{b^2} \left[ 1 + \frac{5\alpha^2}{4} \frac{(Z-l)^2}{b^2} + \frac{21\alpha^4}{8} \frac{(Z-l)^4}{b^4} + \frac{429\alpha^6}{64} \frac{(Z-l)^6}{b^6} \right].$$

We will see later that  $b=2$ , which value has been assumed in calculating the numerical coefficients.

## 18. COMPARISON OF THE THEORY WITH MEASUREMENTS

Sommerfeld\* has thoroughly considered the  $L$ -series (Barkla), of which according to Siegbahn's investigation thirteen lines are known. The wave-numbers of eight of these can be represented by  $L-M$ ,  $L-N$ ,  $L-O$ , etc.,  $L'-M$ ,  $L'-N$ ,  $L'-O$ , etc. They form doublets, viz.,  $L-M$  and  $L'-M$ ,  $L-N$  and  $L'-N$ , etc. Sommerfeld accounts for four of these doublets, viz., the pairs of lines  $(\alpha'\beta)$ ,  $(\gamma\delta)$ ,  $(\epsilon\eta)$ ,  $(\zeta\theta)$ .†

Actually, the differences  $\beta - \alpha'$ ,  $\delta - \gamma$ ,  $\eta - \epsilon$ ,  $\theta - \zeta$  (of which the last does not always occur in the table) are for one and the same element equal to each other (Sommerfeld's Table 3, p. 134, containing thirty-five elements). The table ranges from U ( $Z=92$ ) to Pd ( $Z=46$ ). We have here, for instance,

|       | $\beta - \alpha'$ | $\delta - \gamma$ | $\eta - \epsilon$ | $\theta - \zeta$ |
|-------|-------------------|-------------------|-------------------|------------------|
| 83 Bi | 169.0             | 169.9             | 168.7             | 160.5            |
| 78 Pt | 124.9             | 123.6             | 125.9             | 126.7            |
| 47 Ag | 12.7              | 12.8              |                   |                  |

(The wave-lengths  $\lambda_\beta$  and  $\lambda_{\alpha'}$  are, *e.g.*, for Bi 0.950 and 1.153, for Pt 1.120 and 1.323, for Ag 3.929 and 4.156.)

The theoretical value of the difference  $L' - L = \Delta\nu$  is

$$\Delta\nu = N \frac{\alpha^2(Z-l)^4}{b^4} \left[ 1 + \frac{5}{2} \alpha^2 \frac{(Z-l)^2}{b^2} + \frac{53}{8} \alpha^4 \frac{(Z-l)^4}{b^4} \right],$$

whence,  $N$  and  $a$  being known, the value of

$$\frac{Z-l}{b}$$

can be calculated for each metal. If these numbers are plotted against  $Z$ , the points thus obtained turn out to lie on a straight

\* Cf. the literature at the end of this course of lectures. Sommerfeld's paper therein quoted will, throughout this Article, be referred to with regard to the meaning of the symbols, etc.

† The letters  $\alpha'$ ,  $\beta$ ,  $\gamma$ , etc., are the symbols used by Sommerfeld for the various lines.



line (Sommerfeld's Fig. 5, p. 147), whereas the values which one obtains for  $(Z-l)/b$  without taking account of the relativity correction give a line which is distinctly curved. The values of  $\Delta\nu$  used in this connection are, for each metal, the arithmetical means of  $\beta - \alpha'$ ,  $\delta - \gamma$ , and  $\eta - \epsilon$ .

Now, from the values of  $(Z-l)/b$  for different  $Z$ 's both  $b$  and  $l$  can be determined. (Slope of the straight line and its intersection point with the  $Z$ -axis.) This gave  $b = 2.000 \pm 0.005$  and  $l = 3.5 \pm 0.02$ . In estimating the possible errors it has been taken into account that  $\delta a/a$  is at the utmost  $\pm 0.004$ , the value of  $a$  being derived from Paschen's measurements.

From these results it appears that we must put decidedly  $b = 2$ , while  $l$  is certainly not a whole number.

The four lines  $\epsilon$ ,  $\alpha'$ ,  $\gamma$ ,  $\zeta$  have thus the meaning :

$$\epsilon = L - M, \quad \alpha' = L - N, \quad \gamma = L - O, \quad \zeta = L - P,$$

and the lines  $\eta$ ,  $\beta$ ,  $\delta$ , and  $\theta$  are

$$\eta = L' - M, \quad \beta = L' - N, \quad \delta = L' - O, \quad \theta = L' - P.$$

It is worth noticing that the differences  $\Delta\nu$  considered above are all derived from the number  $a$ , and thus from  $\Delta\nu_H$ ,\* notwithstanding that the separations are now very much greater, viz. proportional to  $(Z-l)^4$ . In the case of optical spectra the factor of proportionality was  $Z^4$ , and thus 1 for hydrogen and 16 for helium. Now, for uranium ( $Z=92$ ) it becomes  $(92 - 3.5)^4 = 6 \cdot 10^7$ .

There is yet another remarkable rule which holds approximately. The distance of the two components of a doublet is, approximately,

$$\Delta\nu = N \frac{a^2 Z^4}{b^4}, \text{ i.e. proportional to } Z^4.$$

On the other hand each  $\nu$  is proportional to  $Z^2$ . Now, the wavelength difference of two lines is

$$\Delta\lambda = \lambda_1 - \lambda_2 = \frac{c}{\nu_1} - \frac{c}{\nu_2} = \frac{c\Delta\nu}{\nu_1\nu_2},$$

and therefore independent of  $Z$ . Thus  $\Delta\lambda$  is the same for different elements.

This constancy of  $\Delta\lambda$ , which in Sommerfeld's figure 2, p. 137,

\* Cf Art. 8.



is exhibited for the pairs  $\gamma\delta$ ,  $a'\beta$ ,  $\epsilon\eta$ , is a useful criterion for recognizing pairs of lines which belong to each other.

Sommerfeld illustrates this rule by a few more examples.

Thus, the line  $\alpha$  shows a constant wave-length difference with respect to  $\alpha'$ . This will then be a doublet which must be ascribed, however, to a splitting of the term  $N$ . The line  $\alpha'$  being  $L - N$ , the line  $\alpha$  will be obtained by taking for  $N$  a slightly different value.

Also to  $\beta$  seems to belong a second line  $\beta'$ , which would then form with  $\beta$ ,  $\alpha$ ,  $\alpha'$  a quartet.

Again, among the thirteen lines of the  $L$ -series there are four more, viz.  $\nu$ ,  $\phi$ ,  $\psi$ , and  $\chi$ , of which  $\nu$  and  $\phi$ ,  $\psi$  and  $\chi$  manifestly belong to each other. In fact, the value of  $\Delta\lambda$  for the former as well as for the latter pair remains constant in the series of metals. Moreover,  $\Delta\nu$  is for the pair  $\nu\phi$  the same as for  $\psi\chi$ . For example,

$$\text{Pt. } \phi - \nu = 32.0; \quad \psi - \chi = 31.6.$$

One is thus led to put

$$\begin{aligned} \nu &= \Lambda - M, & \phi &= \Lambda' - M \\ \chi &= \Lambda - N, & \psi &= \Lambda' - N, \end{aligned}$$

where  $\Lambda$  and  $\Lambda'$  are two new terms.

We can say that we have here a  $\Lambda$ -series of doublets. But the difference  $\Lambda - \Lambda'$  cannot be treated in the same way as  $L - L'$ . Since we have to do with doublets, we might be inclined to put  $b=2$ . But how could then  $\Delta\nu$  be four times smaller than the difference  $L - L'$ ? The value of  $Z - l$  would then have to be  $4^{\frac{1}{2}} = 1.4$  times smaller, and thus, *e.g.*, for Pt,  $l$  would no longer be 3.5 but 21, which is much too high.

There seems, besides, to exist a certain connection between the  $L$ -series and the  $\Lambda$ -series. Thus, the  $\theta$ -line of the  $L$ -series and the  $\chi$ -line of the  $\Lambda$ -series form a very narrow doublet with a fairly constant  $\Delta\lambda = 0.004$  for all the elements. The two lines would thus belong to each other, which, however, cannot be explained for the present.

On p. 143, fig. 4, Sommerfeld gives for various metals the position of the lines of the  $L$ -series and the  $\Lambda$ -series. With regard to this we may notice:

1°. That a line of one doublet can very well lie between the components of the other doublet;

2°. That a certain order, such as  $\gamma\beta$ , can very well be reversed in passing from one element to another; also  $\phi\zeta$  shows such a reversal.

After the investigation of the  $L$ -series Sommerfeld succeeded also in analysing completely the  $K$ -series (in which the frequencies are higher). For the line  $K_\alpha$  of this series we have

$$\nu = K - L,$$

whence,  $L$  being known,  $K$  can be found.

Thus, using for  $K$  the formula given above, the value of  $(Z - k)/a$  can be found for each metal. Sommerfeld (Table 8, p. 151) has done this for 17 elements (Siegbahn), from Al (13) to Cs (55). The values thus found being plotted against  $Z$  gave again very nearly a straight line (p. 147). From the slope of this line and its intersection point with the  $Z$ -axis followed  $a = 1$  and  $k = 1.64$ , with an uncertainty  $\delta a = \pm 0.0006$  and  $\delta k = \pm 0.007$ . Thus neither  $k$  nor  $l$  is an integer.

The states of motion  $K$  and  $L$  are herewith completely determined.

We may notice that in thus calculating the  $K$ -term the  $L$ -term had to be much extrapolated, since a line of the  $L$ -series and at the same time one of the  $K$ -series occur only in the case of Cs.

To  $K_\alpha$  belongs a second line  $K_{\alpha'}$ , which forms with it a doublet. The distance of these lines was measured by Malmer between  $Z = 35$  and  $Z = 60$ . The difference  $\Delta\nu$  for this doublet is (Kossel) the same as for the doublets of the  $L$ -series. This follows simply from  $K_\alpha = K - L'$  and  $K_{\alpha'} = K - L$ . We have  $L' > L$  and  $K_{\alpha'} > K_\alpha$ , so that  $K_\alpha$  can well be thus associated with  $L'$ , and  $K_{\alpha'}$  with  $L$ .

There remain still the terms  $M$ ,  $N$ , etc., with which  $K$ ,  $L$  or  $L'$  are to be combined. Also these terms can, up to a certain extent, be determined.

Thus, *e.g.*, we put for the second line of the  $K$ -series

$$K_\beta = K - M_K,$$

calculate  $M_K$  for each element and try to represent it as a function of  $Z$  of the form

$$M_K = N \frac{(Z - p)^2}{c^2}.$$

The relativity correction is here disregarded, because  $c$  is not an integer, so that the present conditions would differ too much from

those of the case to which the relativity theory was originally applied.

Similarly, from  $K_\gamma = K - N_K$ ,  $\epsilon = L - M_L$ ,  $a' = L - N_L$ ,  $\gamma = L - O_L$ ,  $\xi = L - P_L$  one can determine  $N_K$ , etc.

In each of these cases the graphical representation of  $\sqrt{M_K}$ ,  $\sqrt{M_L}$ , etc., as a function of  $Z$  gives, very nearly at least, a straight line, so that the observations are well expressed by the formulae.

Sommerfeld finds for  $M_K$ , etc., the following values of  $p$ ,  $c$ :

|       | $p$  | $c$  |
|-------|------|------|
| $M_K$ | 1.4  | 2.78 |
| $N_K$ | -0.7 | 3.09 |
| $M_L$ | 7.0  | 2.50 |
| $N_L$ | 1.7  | 2.84 |
| $O_L$ | -1.2 | 3.25 |
| $P_L$ | -0.6 | 3.33 |

The  $M$ -series has been measured by Siegbahn. The two strongest lines found by him are  $M_\alpha$  and  $M_\beta$ .

Suppose that

$$M_\alpha = M - N, \quad M_\beta = M - O, \quad M_\gamma = M - P,$$

while, as before,

$$\epsilon = L - M, \quad a' = L - N, \quad \gamma = L - O.$$

Then we should have

$$M_\alpha = a' - \epsilon, \quad M_\beta = \gamma - \epsilon,$$

so that we should be able to represent the lines of the  $M$ -series as combinations of those of the  $L$ -series. This, however, does not seem to be the case. Only  $\xi - \epsilon = M - P$  agrees rather closely with one of Siegbahn's weaker lines. But this may be a chance coincidence.

It will be well to notice that, after all, the  $K$ - and the  $L$ -series differ in type considerably from the Balmer series.

Take, for instance, the lines  $L - M_L$ ,  $L - N_L$ ,  $L - O_L$ ,  $L - P_L$  of the  $L$ -series. Their wave-numbers are, approximately,

$$N \frac{(Z-l)^2}{2^2} - N \frac{(Z-p)^2}{c^2},$$

where  $p$  and  $c$  have the values given above. If  $l$  and  $p$  are neglected, the wave-numbers of these four lines of the  $L$ -series can be put proportional to

$$\frac{1}{2^2} - \frac{1}{2 \cdot 50^2}; \quad \frac{1}{2^2} - \frac{1}{2 \cdot 84^2}; \quad \frac{1}{2^2} - \frac{1}{3 \cdot 25^2}; \quad \frac{1}{2^2} - \frac{1}{3 \cdot 33^2},$$

whereas in the simple case considered by Bohr [Balmer series] the wave-numbers would be proportional to

$$\frac{1}{2^2} - \frac{1}{3^2}; \quad \frac{1}{2^2} - \frac{1}{4^2}; \quad \frac{1}{2^2} - \frac{1}{5^2}; \quad \frac{1}{2^2} - \frac{1}{6^2}.$$

We see that there is a great difference.

While for the hydrogen spectrum the second term can be indefinitely diminished (which corresponds to an ever-increasing radius of the initial circular orbit), this is with the Roentgen rays by no means the case.

To a certain extent this is intelligible. For it is natural to suppose that the motions which we have called  $K, L, M, N, O, P$  are characterised, respectively, by the values  $\frac{h}{2\pi}, \dots, 6\frac{h}{2\pi}$  of the moment of momentum. Now, if this series proceeded still farther, we should arrive at a state of motion for which the moment of momentum would be  $s\frac{h}{2\pi}$  ( $s=7, 8, \dots$ ), and since the orbit is circular, its radius would become

$$r = \frac{1}{mke^2} \cdot \frac{h^2}{4\pi^2 s^2} = \frac{1}{me^2(Z-p)} \cdot \frac{h^2}{4\pi^2 s^2},$$

i.e.

$$r > \frac{1}{me^2 Z} \cdot \frac{h^2}{4\pi^2 s^2}.$$

For a certain value of  $s$  this radius will become greater than the greatest distance at which the electrons lie around the nucleus, and then there is an end to the  $L$ -series (or whatever Roentgen series we may consider).

Of course, we can imagine that one or a few electrons are placed outside the system formed by the nucleus and the remaining electrons. The motion of such external electrons, however, would be governed by a small effective nucleus charge and the corresponding radiation would no longer be Roentgen-radiation but light.

It is rather surprising that, also with regard to the states of motion denoted by  $M$ ,  $N$ , etc., the frequency for a number of elements can be expressed by using the same values of  $p$  and  $c$ .

## 19. ABSORPTION LIMITS AND SECONDARY ROENTGEN RAYS

Sommerfeld deals also with the absorption limits investigated by Wagner. If a Roentgen-spectrum, *e.g.* a continuous one, is thrown upon a thin metal plate with its greatest wave-lengths on the right hand, say, then from the part of the plate which lies to the left of a certain line  $A$  secondary rays are emitted which belong to the characteristic rays of the metal and whose frequency is always smaller than that of the primary radiation. Since the secondary rays have a great intensity, this phenomenon is accompanied by a strong absorption of the incident rays.  $A$  is a sharp limit as regards both the absorption and the secondary radiation. There is a  $K$ -limit, corresponding to the emission of secondary  $K$ -rays, viz.  $K_\alpha$ , and similarly an  $L$ -limit, and even an  $L'$ -limit. We will speak only of the first of these. If, as before,  $K_\alpha$ , etc., stand for wave-numbers, and if  $A$  be the wave-number of the incident rays, then  $A > K_\alpha$ , *i.e.*  $A > K - L'$ . At the same time, however,  $A < K$ . Sommerfeld's interpretation of the last property is as follows:—In the process of absorption an electron must be removed from an orbit lying more inwards to one lying more outwards. This requires a certain work which can only be supplied by incident rays of such a frequency that their energy-element [quantum,  $h\nu$ ] has the necessary magnitude. Now,  $A$  is the least incident frequency; since  $A < K$ , the frequency  $A$  would not suffice to remove the electron to infinity. But Sommerfeld imagines that it is enough to remove it to some finite distance.

## 20. CONCLUDING REMARKS

1. *The combination principle.*—As soon as it was noticed that equal frequency differences occur, the idea of combination vibrations naturally suggested itself; one might think, *e.g.*, on the combination tones in acoustics. This was pointed out in an old investigation by V. A. Julius.\*

In Bohr's theory the combination is brought about in an

\* Cf. literature at the end.

entirely different way ; equal frequency differences arise here by subtracting every two energy values.

2. *The mystery of the emission of radiation* is by no means explained.

This is discussed in Art. 11.

We may add that what is radiated out is not only the energy lost by the electron but also that lost by the nucleus. The latter is, in the case of hydrogen, the 1850th part of the whole output of energy.

## 21. APPLICATION OF THE QUANTUM THEORY TO A MONATOMIC GAS.\* ENTROPY

This interesting application of the quantum theory is due to Planck, whose reasoning we will here briefly reproduce.

Let there be  $N$  molecules in a volume  $V$ . The state of each molecule can be represented by a point in a six-dimensional space  $R_6$ , with the co-ordinates  $x, y, z$  and the momenta  $\xi, \eta, \zeta$  as parameters. Let us divide this space into a number of regions  $g_0, g_1$ , etc., separated by the surfaces  $\sigma_1, \sigma_2$ , etc., which surround each other, in such a way that, if  $S_1, S_2$ , etc., be the regions of  $R_6$  enclosed by these surfaces,

$$g_0 = S_1, \quad g_1 = S_2 - S_1, \quad g_2 = S_3 - S_2, \text{ etc.}$$

Each of the surfaces  $\sigma$  consists of the surface bounding the volume  $V$  and of a spherical surface in the  $\xi, \eta, \zeta$ -space. If  $q$  be the velocity which corresponds to the points of such a spherical surface, the space  $S$  enclosed by it is

$$V \cdot \frac{4}{3} \pi m^3 q^3,$$

and Planck fixes the surfaces  $\sigma_n$  by requiring that

$$\frac{4}{3} \pi V m^3 q^3 = a(nh)^3,$$

where  $a$  is a numerical constant whose value will be given presently. The sizes of the regions  $g_0, g_1, g_2$ , etc., thus become

$$g_n = a\{(n+1)^3 - n^3\}h^3,$$

*i.e.*  $ah^3, \quad ah^3(2^3 - 1^3), \quad ah^3(3^3 - 2^3), \text{ etc.}$

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\* Cf. literature at the end.



All further regions are multiples of  $g_0$ , viz.

$$p_n = \frac{g_n}{g_0} = (n+1)^3 - n^3.$$

The total number  $n$  of regions is very great but finite, it being assumed that  $N \gg n$ .

We suppose that the distribution of the molecules over the regions  $g_0, g_1, g_2, \dots$  is determined by chance, the molecules being, as it were, thrown haphazardly into the phase-space  $R_6$ . If we take as our unit the probability that a molecule shall fall into  $g_0$  and put the probability of its falling into any region proportional to the size of that region, then the probability that  $N_0, N_1, \dots$  assigned molecules shall fall into  $g_0, g_1, \dots$  respectively will be

$$p_0^{N_0} p_1^{N_1} \dots,$$

and therefore, the probability that  $N_0, N_1 \dots$  arbitrary molecules shall fall into these regions,

$$W = p_0^{N_0} p_1^{N_1} \dots \frac{N!}{N_0! N_1! \dots}.$$

The usual causes which bring about Maxwell's law are thus supposed not to be operative within a region  $g_i$ . The distribution within such a region is not governed by the laws of probability. This is a discrepancy in the theory.

We assume that the molecules which fall into the same region are distributed over it uniformly and we can, therefore, attribute to each of them the mean energy belonging to that region. Now, the velocity  $v$  at the boundary of  $g_n$  is proportional to  $n$ , viz. equal to  $\beta n$ , where

$$\beta = \frac{h}{m} \left( \frac{3\alpha}{4\pi V} \right)^{\frac{1}{2}},$$

so that the mean kinetic energy within the region  $g_n$  will be

$$\bar{u}_n = \frac{\int_{n\beta}^{(n+1)\beta} 4\pi v^2 \cdot \frac{1}{2} m v^2 dv}{\int_{n\beta}^{(n+1)\beta} 4\pi v^2 dv} = \frac{\frac{1}{2} m \int_{n\beta}^{(n+1)\beta} v^4 dv}{\int_{n\beta}^{(n+1)\beta} v^2 dv} = \frac{3}{10} m \beta^2 \frac{(n+1)^5 - n^5}{(n+1)^3 - n^3}.$$

Now (since we are concerned only with kinetic energy), the total energy for the above distribution of the molecules over the regions  $g_n$  can be written

$$U = \Sigma N_n \bar{u}_n,$$

where the sum is to be extended from  $n=0$  to  $n=\mathbf{n}-1$ . The value of  $U$  being kept fixed, we ask for the most probable distribution  $N_0, N_1, \dots$ . This will correspond to a maximum of  $\log W$ . We apply Stirling's formula, which gives

$$\begin{aligned} N! &= (2\pi)^{\frac{1}{2}} N^{N+\frac{1}{2}} e^{-N}, \\ N_0! &= (2\pi)^{\frac{1}{2}} N_0^{N_0+\frac{1}{2}} e^{-N_0}, \text{ etc.}, \\ \frac{N!}{N_0! N_1! \dots} &= (2\pi)^{-\frac{1}{2}(\mathbf{n}-1)} \frac{N^{N+\frac{1}{2}}}{N_0^{N_0+\frac{1}{2}} N_1^{N_1+\frac{1}{2}} \dots}. \end{aligned}$$

As already mentioned, we assume  $\mathbf{n}$  to be much smaller than  $N$  and retain of the logarithm of the last expression only

$$N \log N - \sum N_n \log N_n = - \sum N_n \log \frac{N_n}{N}.$$

Thus, putting  $w_n = N_n/N$ , we have

$$\log W = \sum N_n \log p_n - \sum N_n \log w_n$$

or 
$$\log W = -N \sum w_n \log \frac{w_n}{p_n}.$$

Since this is to be a maximum, we have the equation

$$\Sigma \left( \log \frac{w_n}{p_n} + 1 \right) \delta w_n = 0$$

with the supplementary conditions

$$\Sigma \delta w_n = 0 \quad \text{and} \quad \Sigma \overline{u_n} \delta w_n = 0.$$

This gives

$$\log \frac{w_n}{p_n} = c' - \overline{c u_n},$$

where  $c$  and  $c'$  are constants. Thus,

$$w_n = a p_n e^{-\overline{c u_n}}.$$

The constants  $a$  and  $c$  are to be determined from the conditions

$$\sum w_n = 1,$$

$$\sum w_n \overline{u_n} = \frac{U}{N}.$$

Thus,

$$\frac{1}{a} = \sum p_n e^{-\overline{c u_n}},$$

while  $c$  will be determined by

$$\frac{\sum p_n \overline{u_n} e^{-\overline{c u_n}}}{\sum p_n e^{-\overline{c u_n}}} = \frac{U}{N}. \quad \dots \quad (51)$$

The value of  $W$  corresponding to this most probable distribution will now be given by

$$\begin{aligned}\log W &= -N \Sigma (c' - \overline{cu_n}) w_n = -N \log a + N c \frac{U}{\bar{N}} \\ &= N \log \Sigma p_n e^{-\overline{cu_n}} + cU.\end{aligned}$$

The entropy  $S$  being defined by

$$S = k \log W,$$

we have for the entropy in the most probable state

$$S = kN \log (\Sigma p_n e^{-\overline{cu_n}}) + kcU. \quad . \quad . \quad . \quad (52)$$

We will now express the entropy in terms of the energy and the volume, the usual independent variables.

Suppose that the energy increases by  $dU$ . Then  $S$  will increase by

$$dS = \frac{1}{T} dU.$$

But, when  $U$  is varied, also  $c$  changes. Thus,

$$dS = -kN \frac{\Sigma p_n e^{-\overline{cu_n}} \overline{u_n} dc}{\Sigma p_n e^{-\overline{cu_n}}} + kU dc + kcdU,$$

or, by (51),

$$dS = kcdU,$$

so that

$$c = \frac{1}{kT}.$$

Consequently the entropy becomes

$$S = kN \log \Sigma p_n e^{-\frac{\overline{u_n}}{kT}} + \frac{1}{T} U,$$

and is thus determined as a function of the energy and the volume. At the same time we have, by (51),

$$U = N \frac{\Sigma p_n \overline{u_n} e^{-\frac{\overline{u_n}}{kT}}}{\Sigma p_n e^{-\frac{\overline{u_n}}{kT}}}.$$

## 22. FREE ENERGY AND THERMODYNAMICAL FUNCTION

Planck considers also the free energy  $F$  and a thermodynamical function  $\Psi = -F/T$ .

By what precedes,

$$F = U - TS = -kNT \log \sum p_n e^{-\frac{\bar{u}_n}{kT}}$$

and 
$$\Psi = -\frac{F}{T} = -\frac{U}{T} + S = kN \log \sum p_n e^{-\frac{\bar{u}_n}{kT}}.$$

As is well known,

$$\frac{\partial F}{\partial V} = -p, \quad \frac{\partial F}{\partial T} = -S.$$

Thus, since  $F = -\Psi T$ ,

$$-\Psi - T \frac{\partial \Psi}{\partial T} = -S; \quad \frac{F}{T} - T \frac{\partial \Psi}{\partial T} = -S,$$

$$T^2 \frac{\partial \Psi}{\partial T} = F + TS$$

or

$$U = T^2 \frac{\partial \Psi}{\partial T},$$

$$S = -\frac{F}{T} + \frac{U}{T} = \Psi + T \frac{\partial \Psi}{\partial T}.$$

We have still to substitute in  $\Psi$  the values of  $p_n$  and  $\bar{u}_n$ . First, we have

$$p_n = (n+1)^3 - n^3.$$

Next,

$$\frac{\bar{u}_n}{kT} = \frac{(n+1)^5 - n^5}{(n+1)^3 - n^3} \sigma,$$

where

$$\sigma = \frac{3}{10} \frac{h^2}{mkT} \left( \frac{3a}{4\pi V} \right)^{\frac{3}{2}}.$$

Thus,

$$\Psi = kN \log \sum [(n+1)^3 - n^3] e^{-\frac{(n+1)^5 - n^5}{(n+1)^3 - n^3} \sigma}$$

The number  $a$  remains still undetermined. Now, when at a constant temperature the volume  $V$  and the number of molecules  $N$  are increased in the same ratio, also  $\Psi$  must increase in this ratio, so that  $\sigma$  must remain constant. To ensure this, Planck makes  $a$  proportional to  $N$ , putting, that is,

$$a = \frac{N}{e},$$

where  $e$  is the base of natural logarithms.\* Thus  $\sigma$  becomes

$$\sigma = \frac{3}{10} \frac{h^2}{mkT} \left( \frac{3}{4\pi ev} \right)^{\frac{2}{3}},$$

where  $v = V/N$ .

We will now consider some peculiarities of this gas model.

The pressure is determined by

$$p = - \frac{\partial F}{\partial V} = T \frac{\partial \Psi}{\partial V},$$

while the energy is

$$U = T^2 \frac{\partial \Psi}{\partial T}.$$

Is the pressure equal to two-thirds of the energy per unit volume?

This would mean

$$T \frac{\partial \Psi}{\partial V} = \frac{2}{3} T^2 \frac{\partial \Psi}{\partial T} \cdot \frac{1}{V}$$

or

$$V \frac{\partial \Psi}{\partial V} = \frac{2}{3} T \frac{\partial \Psi}{\partial T},$$

and such indeed is the case, since  $\Psi$  is a function of  $TV^{\frac{2}{3}}$ .

### 23. ZERO-POINT ENERGY

The formulae derived above lead to a zero-point energy.

In fact, when  $T$  tends to zero, all molecules fall into  $g_0$ . The total energy then becomes

$$\begin{aligned} U_0 = N u_0 &= \frac{3}{10} m \beta^2 N = \frac{3}{10} \frac{h^2}{m} \left( \frac{3a}{4\pi V} \right)^{\frac{2}{3}} N \\ &= \frac{3}{10} \frac{h^2}{m} \left( \frac{3N}{4\pi e V} \right)^{\frac{2}{3}} N = \frac{3}{10} \frac{h^2}{m} \left( \frac{3}{4\pi e} \right)^{\frac{2}{3}} \frac{N^{\frac{5}{3}}}{V^{\frac{1}{3}}}, \end{aligned}$$

and therefore, the energy per unit volume,

$$\gamma \left( \frac{N}{V} \right)^{\frac{5}{3}},$$

where  $\gamma = \frac{3}{10} \frac{h^2}{m} \left( \frac{3}{4\pi e} \right)^{\frac{2}{3}}$ , and the pressure becomes

$$p = \frac{2}{3} \gamma \left( \frac{N}{V} \right)^{\frac{5}{3}}.$$

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\* In Planck's presentation of the theory occurs  $N!$  which he replaces by  $(N/e)^N$ . This gives rise to the expression  $N/e$  which we have denoted by  $a$ .

## 24. ADIABATIC EXPANSION AT THE ABSOLUTE ZERO

For an isothermal expansion at  $T=0$  we have

$$pdV = \frac{2}{3}\gamma \frac{N^{\frac{2}{3}}}{V^{\frac{2}{3}}}dV, \quad dU = -\frac{2}{3}\gamma \frac{N^{\frac{2}{3}}}{V^{\frac{2}{3}}}dV,$$

and therefore,

$$pdV = -dU,$$

whence we see that this expansion requires no heat supply, and is thus always an adiabatic expansion. Conversely, in an adiabatic expansion at the absolute zero the temperature remains zero. It is true that owing to the work done by the gas the energy diminishes, but the zero-point energy depends on the volume in such a way that the decreased energy is just the zero-point energy corresponding to the increased volume. The temperature zero remains also unaltered in an adiabatic compression.

These properties are connected with the fact that the entropy at  $T=0$  is independent of the volume, its value being always zero (cf. Art. 27).

If the gas, at  $T=0$ , expands suddenly by rushing into a vacuum, its temperature rises.

## 25. FLUCTUATIONS OF DENSITY

It is worth while to consider also the fluctuations of the density in a gas. For this purpose we will start from a general formula. If  $\Delta\rho$  is the deviation from the normal density  $\rho$  in a volume  $v$  which is a very small fraction of the total volume, then, according to ordinary statistical mechanics,

$$(\overline{\Delta\rho})^2 = \frac{kT\rho}{v} : \frac{\partial\rho}{\partial p},$$

where the pressure  $p$  is to be considered as a function of  $\rho$  and  $T$ . If we have to do with the usual perfect gas, then, if  $n$  be the average number of molecules per unit volume and  $nv + \nu$  the number of molecules in the volume  $v$ ,

$$\Delta\rho = \frac{m}{v}\nu, \quad \rho = mn, \quad p = kTn = kT \frac{\rho}{m}, \quad \frac{\partial p}{\partial \rho} = \frac{kT}{m}.$$



If these values are substituted into the formula for  $(\overline{\Delta\rho})^2$ , then

$$\nu^2 = nv, \quad . \quad . \quad . \quad . \quad . \quad (53)$$

a well-known result, which could also be found directly by noticing that the probability for a molecule to fall, independently of all other molecules, into the volume  $v$  is given by the ratio of  $v$  to the total volume. If one calculated  $\partial p / \partial \rho$  by means of Planck's formula, one would have arrived at a different result. In fact, it can readily be shown that the relation (53) can hold only if the gas satisfies the usual equation of state for an ideal gas. For, from that relation follows

$$(\overline{\Delta\rho})^2 = \frac{m^2}{v^2} \nu^2 = \frac{m^2 n}{v} = \frac{m\rho}{v},$$

and if this be substituted into the formula for  $(\overline{\Delta\rho})^2$ , we have

$$\frac{\partial p}{\partial \rho} = \frac{kT}{m},$$

and therefore, since  $p=0$  for  $\rho=0$ ,

$$p = kT \frac{\rho}{m} = kT n. \quad . \quad . \quad . \quad . \quad (54)$$

Thus, since the assumption of mutual independence of the molecules leads necessarily to (53) and therefore also to (54), such an assumption is incompatible with Planck's formula. On the other hand, one does not see at all how the molecules should act upon each other.

For it is certainly impossible to suppose that the mutual action of the molecules consists in anything like a collision between them. In fact, let us imagine in the given volume  $V$  a number  $N$  of molecules with a given total energy  $U$ . This state of the system, which we will call the state 1, will be characterised by a certain distribution, the regions  $g_0, g_1$ , etc., containing given numbers of molecules,  $N_0, N_1$ , etc. Now, the state 1, being once attained, could persist also without the collisions between the molecules. The collisions are not necessary for keeping it up.

In fact, it is not difficult to see that not only each region  $g_n$  but also each of the elements  $dg$  into which the phase-space can be divided will permanently contain the same molecules. Thus, not only does each  $g_n$  contain a constant number of molecules, but these molecules remain also uniformly distributed over  $g_n$ .

Now, suppose that the interaction between the molecules which we must assume consists in collisions, two by two. Then any element  $dg$  must gain through the collisions as many molecules as it loses. But since the state 1 is thus maintained, we should get also a stationary state by doubling the number of molecules in each element  $dg$ . For then all the numbers of collisions would be quadrupled and each element would still gain as many molecules as it loses.

We should then have for a gas of twice the original density a distribution with the same elementary regions  $g_0, g_1$ , etc. Such a state, however, is, according to Planck's theory, impossible. For the elementary regions are separated from each other by the spheres

$$\frac{4}{3}\pi Vm^3q^3 = \alpha(nh)^3,$$

and since  $\alpha$  had to be made proportional to  $N$ , the boundaries of these regions will not remain unaltered when the density is increased.

## 26. THE EFFECT OF GRAVITY

It is interesting to consider a gas under the action of gravity. This can again serve to show that in Planck's theory some interaction between the molecules must necessarily be assumed.

In fact, consider the case of equilibrium under the assumption that there is no interaction between the molecules.

Let  $\xi, \eta, \zeta$  be the velocity components of a molecule and  $X, Y, Z$  the components of an external force acting upon the molecule. Then the distribution function  $f=f(x, y, z, \xi, \eta, \zeta)$  for a stationary state satisfies the fundamental equation of the kinetic theory,

$$\xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} + \frac{X}{m} \frac{\partial f}{\partial \xi} + \frac{Y}{m} \frac{\partial f}{\partial \eta} + \frac{Z}{m} \frac{\partial f}{\partial \zeta} = 0,$$

or, if the external forces are conservative and if  $\phi$  be the corresponding potential energy,

$$\xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} - \frac{1}{m} \left( \frac{\partial \phi}{\partial x} \frac{\partial f}{\partial \xi} + \frac{\partial \phi}{\partial y} \frac{\partial f}{\partial \eta} + \frac{\partial \phi}{\partial z} \frac{\partial f}{\partial \zeta} \right) = 0,$$

Suppose now that, as in the usual theory of gases and also in

Planck's theory,  $f$  depends only on  $x, y, z$ , and  $u = \frac{1}{2}m(\xi^2 + \eta^2 + \zeta^2)$ . Then

$$\frac{\partial f}{\partial \xi} = m\xi \frac{\partial f}{\partial u}, \quad \frac{\partial f}{\partial \eta} = m\eta \frac{\partial f}{\partial u}, \quad \frac{\partial f}{\partial \zeta} = m\zeta \frac{\partial f}{\partial u}$$

and the fundamental equation becomes

$$\xi \left( \frac{\partial f}{\partial x} - \frac{\partial \phi}{\partial x} \frac{\partial f}{\partial u} \right) + \eta \left( \frac{\partial f}{\partial y} - \frac{\partial \phi}{\partial y} \frac{\partial f}{\partial u} \right) + \zeta \left( \frac{\partial f}{\partial z} - \frac{\partial \phi}{\partial z} \frac{\partial f}{\partial u} \right) = 0.$$

Since this has to be satisfied for all values of  $\xi, \eta, \zeta$ , we must have

$$\frac{\partial f}{\partial x} = \frac{\partial \phi}{\partial x} \frac{\partial f}{\partial u}, \quad \frac{\partial f}{\partial y} = \frac{\partial \phi}{\partial y} \frac{\partial f}{\partial u}, \quad \frac{\partial f}{\partial z} = \frac{\partial \phi}{\partial z} \frac{\partial f}{\partial u}.$$

For a fixed value of  $u$  the derivatives  $\partial f / \partial x$ , etc., are, throughout the space  $x, y, z$ , proportional to  $\partial \phi / \partial x$ , etc., so that  $f$  must then be a function of  $\phi$ . In general, therefore,  $f$  is a function of  $\phi$  and  $u$ , and the last three equations are reduced to

$$\frac{\partial f}{\partial \phi} = \frac{\partial f}{\partial u},$$

so that the distribution function must be of the form

$$f(u + \phi) = f(\tfrac{1}{2}mq^2 + \phi),$$

where  $q$  is the velocity.

Now, suppose that at a certain level [more generally, at a certain place]  $f$  is discontinuous for certain values  $q_1, q_2, q_3$ , etc., of  $q$ . Then at another level  $f$  must be discontinuous for certain other values  $q'_1, q'_2, q'_3$ , etc., such that

$$\tfrac{1}{2}mq_n^2 + \phi = \tfrac{1}{2}mq'_n{}^2 + \phi'$$

$$\text{or} \quad q_n^2 - q'_n{}^2 = \frac{2}{m}(\phi' - \phi). \quad (55)$$

But the right-hand member is independent of  $n$ . Thus, when we move up or down the gas column, the discontinuities of  $q^2$  would all be changed by *the same* amount. This, however, would clash with Planck's theory, according to which the discontinuities are determined by

$$\frac{4}{3}\pi V m^3 q_n^3 = \alpha (n\hbar)^3 = \frac{N}{e} (n\hbar)^3$$

$$\text{or} \quad q_n^3 \propto \frac{N}{V} n^3 \propto \rho n^3,$$

$$\text{i.e.} \quad q_n \propto n\rho^{\frac{1}{3}}. \quad (56)$$

Now, this result agrees with (55) in so far as according to both formulae the values of  $q_n$  decrease when we move upwards. But, in contradiction with what we have derived from (55), it follows from (56) that, when  $p$  changes by a certain amount, the various discontinuity values of  $q_n^2$  do not all change by the same amount. On the contrary, the amount of change is proportional to  $n^2$ . Thus, if in treating the effect of gravity one disregards all mutual action of the molecules, one is led to a result which clashes with Planck's theory.

## 27. FURTHER REMARKS ON PLANCK'S THEORY. CHEMICAL CONSTANT

There is, besides, much about Planck's theory that is arbitrary. Thus, for example, we might as well have assumed that the limits of the regions are determined by

$$\frac{4}{3}\pi V m^3 q_n^3 = N f(n) h^3,$$

leaving the form of the function  $f(n)$ \* (for  $n=1, 2, 3$ , etc.) undetermined and requiring only that it should always increase with increasing  $n$  and that  $f(0)=0$ .

This would give for the elementary regions

$$g_n = N \{f(n+1) - f(n)\} h^3,$$

$$p_n = \frac{g_n}{g_0} = \frac{f(n+1) - f(n)}{f(1)},$$

whence 
$$\bar{u}_n = \frac{3}{10} \frac{h^2}{m} \left( \frac{3N}{4\pi V} \right)^{\frac{2}{3}} \frac{[f(n+1)]^{\frac{5}{3}} - [f(n)]^{\frac{5}{3}}}{f(n+1) - f(n)},$$

$$\Psi = kN \log \Sigma \left\{ \frac{f(n+1) - f(n)}{f(1)} e^{-\sigma \frac{[f(n+1)]^{\frac{5}{3}} - [f(n)]^{\frac{5}{3}}}{f(n+1) - f(n)}} \right\},$$

$$\sigma = \frac{3}{10} \frac{h^2}{mkT} \left( \frac{3N}{4\pi V} \right)^{\frac{2}{3}}.$$

The zero-point energy, averaged for a molecule, would be

$$\bar{u}_0 = \frac{3}{10} \frac{h^2}{m} \left( \frac{3N}{4\pi V} \right)^{\frac{2}{3}} [f(1)]^{\frac{5}{3}}.$$

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\* Which was before  $f(n) = \frac{1}{e} n^3$ .

For very high temperatures  $T$  we get the usual velocity distribution obeying Maxwell's law.

In fact, when  $T$  is large, we have mainly to do with high values of  $n$ . Let us assume that for large  $n$  the ratio  $f(n+1):f(n)$  differs but little from 1. Then also the ratio of two successive values of  $q_n$  will differ but little from 1, so that the discontinuities will disappear.

Now, as we saw before,

$$w_n = \frac{N_n}{N} = ap_n e^{-\frac{u_n}{kT}},$$

and since  $p_n$  is proportional to the size of an elementary region, the density is proportional to  $e^{-\frac{u_n}{kT}}$  or, as we can say, proportional to  $e^{-\frac{u}{kT}}$ . Thus we come to Maxwell's law.

In connection with the disappearance of the discontinuities Planck replaces the expression for the thermodynamical function  $\Psi$  at high temperatures by an integral.

Since

$$f(n) = \frac{4}{3} \pi \frac{V}{N} \frac{m^3}{h^3} q^3,$$

we can put

$$f(n+1) - f(n) = 4\pi \frac{V}{N} \frac{m^3}{h^3} q^2 dq,$$

where  $dq$  is the velocity interval corresponding to an elementary region. This gives

$$\begin{aligned} \Psi &= kN \log \int_0^\infty \frac{4\pi V m^3}{N h^3 f(1)} q^2 dq e^{-\frac{mq^2}{2kT}} \\ &= kN \log \left\{ \frac{4\pi V m^3}{N h^3 f(1)} \cdot \frac{1}{4} \sqrt{\frac{8\pi k^3 T^3}{m^3}} \right\} \\ &= \frac{3}{2} kN \log \left\{ \frac{2\pi k m T}{h^2} \left( \frac{V}{N f(1)} \right)^{\frac{3}{2}} \right\}, \end{aligned}$$

which for  $f(1)=1/e$  reduces to a formula derived by Planck. If we put

$$\frac{2\pi k m}{h^2} [N f(1)]^{-\frac{3}{2}} = \beta,$$

then

$$\Psi = \frac{3}{2} kN \log (\beta V^{\frac{3}{2}} T),$$





where  $g = G/N$  and  $G$  is an elementary region introduced as a constant. If we put

$$p = \frac{2}{3} \frac{U}{V},$$

then  $S = kN \left( \log V + \frac{5}{2} \log T - \log U + \text{const.} \right)$ .

In Planck's book, *Theorie der Wärmestrahlung*, we find

$$S = kN \log \left\{ \frac{V}{G} \left( \frac{4\pi em(E - E_0)}{3N} \right)^{\frac{3}{2}} \right\},$$

where  $E - E_0$  is the energy of the translational motion of the molecules, while  $E_0$ , supposed to be invariable, is their internal energy.

It is worth noticing that Planck's new theory leads to the formula (58) for high temperatures only. For low temperatures the result deviates from that expression and the theory introduces far-reaching changes into the formulae for gases.

The values yielded for the entropy of a gas at the absolute zero of temperature by Planck's older theories and his new theory differ greatly from each other, being  $-\infty$  and 0 respectively. In fact, we have, according to the new theory,

$$\Psi = kN \log \Sigma [(n+1)^3 - n^3] e^{-\frac{(n+1)^5 - n^5}{(n+1)^3 - n^3} \sigma},$$

where  $\sigma \propto 1/T$ . If  $T$  is small, and therefore  $\sigma$  large, the term with  $n=0$  predominates over all others, and we are left with

$$\Psi = kN \log e^{-\sigma} = -kN\sigma.$$

Now, the entropy is

$$S = \Psi + T \frac{\partial \Psi}{\partial T} = -kN \left( \sigma + T \frac{\partial \sigma}{\partial T} \right),$$

and this is nil, since  $\sigma$  is proportional to  $1/T$ .

One of the phenomena in which the value of the constant  $a$  manifests itself is the vapour pressure ( $p$ ) of a solid or a liquid phase.

Let  $S'$  be the entropy of this phase and  $S$  that of the vapour, both taken for a gram molecule, and let  $v'$  and  $v$  be the volumes.

Then

$$S - S' = (v - v') \frac{dp}{dT},$$

which can as well be written

$$S - S' = v \frac{dp}{dT}$$

or, putting  $v = RT/p$ ,

$$S - S' = RT \frac{d \log p}{dT}. \quad (60)$$

Now, according to (59),

$$S = R \log v + \frac{3}{2} R \log \left( \frac{3}{2} RT \right) + a,$$

and substituting  $v = RT/p$ ,

$$\begin{aligned} S &= R \log (RT) - R \log p + \frac{3}{2} R \log \left( \frac{3}{2} RT \right) + a \\ &= \frac{5}{2} R \log (RT) - R \log p + \frac{3}{2} R \log \frac{3}{2} + a, \end{aligned}$$

$$\text{or, putting } \frac{5}{2} R \log R + \frac{3}{2} R \log \frac{3}{2} = b,$$

$$S = a + b + \frac{5}{2} R \log T - R \log p.$$

If this is introduced into (60), we have

$$a + b + \frac{5}{2} R \log T - R \log p - S' = RT \frac{d \log p}{dT}, \quad (61)$$

an equation for  $p$  as function of  $T$ . This can also be written

$$R \frac{d}{dT} (T \log p) = a + b - S' + \frac{5}{2} R \log T, \quad (62)$$

whence  $a$  can be determined.

Example.—The vapour pressure over liquid mercury is, according to Hertz, given by

$$\log p = 10.59271 - 0.847 \log T - \frac{3342}{T},$$

in common (Briggsian) logarithms and with  $\bar{p}$  written for the vapour pressure in mm. mercury. Since 1 mm. mercury corresponds to 1330 dynes per cm.<sup>2</sup>, we have to put  $p = 1330 \bar{p}$ , so that

$$\log p = 13.716 - 0.847 \log T - \frac{3342}{T}.$$

To pass from common to natural logarithms we have to multiply by 2.3026. Ultimately, therefore,

$$\log p = \alpha - \beta \log T - \frac{\gamma}{T},$$

where  $\alpha = 31.583$ ,  $\beta = 0.847$ ,  $\gamma = 7697$ . Whence

$$\frac{d}{dT}(T \log p) = (\alpha - \beta) - \beta \log T.$$

Let us evaluate this expression for the melting point of mercury (or rather its triple point),  $T = 234$ . I find

$$\frac{d}{dT}(T \log p) = 26.12.$$

To apply (62), we still require  $S'$ , the entropy of a gram molecule of liquid mercury.

Consider first solid mercury. If we imagine that this is heated under the constant pressure  $p$  from  $0^\circ$  to  $T$ , we shall have for the entropy, which by assumption is zero for  $T = 0$ ,

$$\int_0^T \frac{c_p}{T} dT.$$

From the data given by Nernst (based on Pollitzer's observations) I find for this expression, with  $T = 234$ ,

$$6.95 R.$$

To get  $S'$  for the liquid mercury, we have to add to this the value of  $r/T$ , where  $r$  is the heat of melting (in ergs) per gram molecule. This is, in calories, 554, and therefore, in ergs,

$$2316 \times 10^7 = 277R \text{ (since } R = 83.2 \cdot 10^6),$$

so that 
$$\frac{r}{T} = 1.18R.$$

Thus 
$$S' = 8.13R,$$

and equation (62) becomes

$$\frac{a}{R} = 34.25 - \frac{5}{2} \log T - \frac{b}{R}. \quad (63)$$

Now, we have found before

$$a = R \left[ -\frac{5}{2} \log N - \log f(1) + \frac{3}{2} \log \left( \frac{4\pi me}{3h^2} \right) \right],$$

$$b = \frac{5}{2} R \log R + \frac{3}{2} R \log \frac{3}{2}.$$

Substituting these values, with  $f(1) = 1/e$ ,  $\log f(1) = -1$ , into (63), we find, after simple reductions,

$$\log (h^2) = \log (2\pi m) - \frac{5}{3} \log \frac{N}{RT} - 21.17.$$

This is in natural logarithms. Thus, in Briggsian logarithms,

$$\log (h^2) = \log (2\pi m) - \frac{5}{3} \log \frac{N}{RT} - 9.19.$$

If we take  $1.64 \cdot 10^{-24}$  gr. for the mass of a hydrogen atom, that of a mercury atom will be  $328 \cdot 10^{-24}$ . With this value of  $m$ , and with

$$N = 61 \cdot 10^{22}, R = 83.2 \cdot 10^6, T = 234,$$

the last formula gives

$$h = 6.5 \cdot 10^{-27}.$$

It is certainly remarkable that one arrives in this way at a number which is in good agreement with the value deduced from radiation phenomena,  $h = 6.4 \cdot 10^{-27}$ .

Had we taken  $\log f(1) = -2$  instead of  $-1$ , the result would be  $h = 9.1 \cdot 10^{-27}$ .

It is interesting to integrate the differential equation (62). One finds

$$R \log p = a + b - \frac{1}{T} \int_0^T S' dT + \frac{5}{2} R (\log T - 1) - \frac{c}{T}, \quad (64)$$

where  $c$  is an integration constant. We thus see how the constant  $a$  enters into the formula for  $\log p$ . In order to find the physical significance of the constant  $c$  we make use of the relation

$$U - U' = T(S - S') - RT$$

or, by (60),

$$U - U' = RT^2 \frac{d \log p}{dT} - RT.$$

Now, by (64),

$$R \frac{d \log p}{dT} = \frac{1}{T^2} \int_0^T S' dT - \frac{S'}{T} + \frac{5}{2} \frac{R}{T} + \frac{c}{T^2}.$$

Consequently,

$$U - U' = \int_0^T S' dT - S'T + \frac{3}{2} RT + c.$$

When  $T$  tends to zero,  $U - U'$  tends to  $c$ .

Thus  $c$  is connected with the work which must be done in order to bring a molecule from the solid into the vapour phase.

## 28. EQUILIBRIUM BETWEEN TWO PHASES

In this theory there is something which is not quite satisfactory. If we have a substance, such as mercury, which can occur in different states, we may consider the entropies belonging to these states. According to classical thermodynamics we then have to do only with *entropy differences*. Now, it is clear that, without altering any of these differences, the entropy for a single state can be given an arbitrary value, say zero. Thus the essential feature of the new treatment is not that we fix the entropy in one state; the novelty comes in only when we do this for *two* states, as *e.g.* when we require, in accordance with Nernst's theorem, that two solid phases which can pass into each other (such as two allotropic forms) shall have at the absolute zero-point the same entropy, which can then be made 0.

Such a disposal will always need a discussion as to its legitimacy. Now, in the theory which we have just considered the entropy was indeed fixed twice, namely, first, when we equated it to zero for solid mercury at the absolute zero-point, and then when applying the quantum hypothesis to a monatomic gas we have attributed to its entropy a perfectly definite numerical value.

The question ultimately is whether these two acts of fixing the entropy do not perhaps disagree with each other. No attention was paid to this question, because in fixing the entropy for the first phase one scarcely thought of the other. I do not wish to imply that a mistake has been made, but only that the fixing of the entropy needs a further justification.

Roughly, such a justification can be formulated as follows. Suppose we have two phases  $P_1$  and  $P_2$  with the corresponding energy values  $U_1$  and  $U_2$ . The phase  $P_1$ , while having a definite energy, can still occur in very different states; let  $W_1$  be the number of these elementary states. This will be a certain function of  $U_1$ . Let  $W_2$  have a similar meaning for the second phase. Then the fundamental hypothesis which connects one phase with the other is that, taken in itself, each combination of an elementary state of the first phase with one of the second phase is equally probable. Now, if the two phases are in contact with each other, the total energy  $U$  which we assume as

given can still be distributed over the two phases in various ways. The two energies can be  $U_1$ ,  $U_2$ , say, or  $U'_1$ ,  $U'_2$ , provided that  $U_1 + U_2 = U$  and  $U'_1 + U'_2 = U$ . Then, by our hypothesis, the probabilities of the distribution  $U_1$ ,  $U_2$  and  $U'_1$ ,  $U'_2$  are to each other as the products  $W_1 W_2$  and  $W'_1 W'_2$ . The most probable distribution will thus be determined by the condition that  $W_1 W_2$  or, if we put  $k \log W = S$ , that  $S_1 + S_2$  shall be a maximum. This gives the condition

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2},$$

say, both  $= 1/T$ .

But this is not all. To complete the investigation of the equilibrium of the two phases we must still consider the possibility of a passage from one to the other. Let  $M$  be the total mass, of which  $m_1$  is in the first, and  $m_2$  in the second phase. If the total energy  $U$  be again given, we can find its most probable distribution for given  $m_1$  and  $m_2$ , and thus determine the most probable values of  $U_1$  and  $U_2$ . These will be functions of  $m_1$  (by which also  $m_2$  is determined) or of  $m_2$ . At the same time we find also the product  $W_1 W_2$  of the numbers  $W_1$  and  $W_2$  corresponding to these energy values as a function of  $M$  and  $m_1$ . Thus to the distributions  $m_1$ ,  $m_2$  and  $m'_1$ ,  $m'_2$  will correspond the numbers  $W_1 W_2$  and  $W'_1 W'_2$  of combinations of elementary states by which these distributions can be realised, and if we assume that the probabilities of  $m_1$ ,  $m_2$  and  $m'_1$ ,  $m'_2$  are proportional to these numbers, we need only to ask for what values of  $m_1$ ,  $m_2$  the product  $W_1 W_2$  or the sum  $S_1 + S_2$  becomes a maximum. This gives

$$\frac{\partial S_1}{\partial m_1} = \frac{\partial S_2}{\partial m_2}$$

as the condition for the equilibrium between the two phases so far as the passage of matter from one into the other is concerned. But if these assumptions concerning their mutual equilibrium be granted, we can fix the elementary states separately for either phase without coming to contradictions. Thus, for instance, we can speak in the case of a solid phase of the various ways in which the energy can be distributed in quanta over the possible types of motion, and in the case of a gas, of the different distributions of the molecules over the elementary regions of the phase-space.



## 29. DISSOCIATION

The "chemical constant" of a gas which made its appearance in the theory of the vapour pressure plays also a certain rôle in other physical and chemical equilibria in which one or more gases take part, as, for instance, in the dissociation equilibrium of solid phases which give out a gaseous constituent,\* or in the dissociation equilibrium of entirely gaseous systems. The latter case has been investigated, in a very ingenious way, mainly by Nernst and his pupils. The theory of such gas equilibria will now be briefly considered.

In dealing with a gas we can consider the entropy  $s$  of a gram molecule as function of the energy  $u$  and the volume  $v$ . If for constant energy, and thus also at constant temperature (each gas being treated as "ideal"), the volume increases by  $dv$ , the entropy will increase by  $\frac{p}{T}dv = R\frac{dv}{v}$ . Thus, if  $s$  stands in particular for the entropy corresponding to the energy  $u$  and the volume 1, the general value of the entropy can be written [per gram molecule]

$$s + R \log v.$$

If the volume  $v$  contains  $n$  gram molecules, the entropy is

$$ns + Rn \log \frac{v}{n}.$$

Finally, if the volume  $v$  contains  $n_1, n_2$ , etc., gram molecules of different gases, for which  $u$  and  $s$  have the values  $u_1, u_2$ , etc.,  $s_1, s_2$ , etc., the total entropy is (Gibbs' theorem)

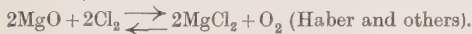
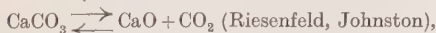
$$S = \Sigma \left( ns + Rn \log \frac{v}{n} \right),$$

each gas contributing a term to the sum.

Similarly, the total energy is  $U = \Sigma nu$ .

Keeping the volume  $v$  and the total energy  $U$  constant we

\* For example,



will derive from the condition  $S = \text{maximum}$  the most probable distribution of energy over the various gases as well as the most probable quantity of each of these. In fact, by a chemical reaction the gases can pass into each other. Writing such a reaction, say  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$ , in the form  $2\text{H}_2 + \text{O}_2 - 2\text{H}_2\text{O} = 0$  and denoting the positive or negative coefficients which occur for the several gases by  $a_1, a_2$ , etc. (as, *e.g.*, 2, 1, -2), we can speak of a possible reaction in which the numbers  $n_1, n_2$ , etc., undergo the changes  $a_1, a_2$ , etc., or changes proportional to these coefficients.

Let an infinitesimal change of the system be defined by the variations  $\delta u_1, \delta u_2$ , etc., and, as regards chemical reaction, by  $\delta n_1 = a_1 \epsilon, \delta n_2 = a_2 \epsilon$ , etc., where  $\epsilon$  is infinitesimal. Then we have the condition  $\delta S = 0$ , and since  $s$  for each gas depends on  $u$ ,

$$\Sigma \left[ n \frac{\partial s}{\partial u} \delta u + \left( s + R \log \frac{v}{n} - R \right) a \epsilon \right] = 0,$$

with the supplementary condition  $\delta U = 0$  or

$$\Sigma [n \delta u + u a \epsilon] = 0.$$

We multiply the second equation by  $C$ , add it to the first, and equate to zero the coefficient of each  $\delta u$  and of  $\epsilon$ . The former gives

$$\frac{\partial s}{\partial u} + C = 0, \quad C = -\frac{1}{T},$$

and the latter,

$$\Sigma \left[ \left( s + R \log \frac{v}{n} - R \right) a - \frac{u}{T} a \right] = 0$$

or, dividing by  $R$ ,

$$\Sigma \log \left( \frac{n}{v} \right)^a = \frac{1}{R} \Sigma a \left( s - \frac{u}{T} \right) - \Sigma a. \quad . \quad . \quad . \quad (65)$$

Notice that this equation remains unaltered if  $a_1, a_2$ , etc., are all multiplied by the same number or, in particular, if their signs are inverted.

From (65) we see that for a given temperature and volume  $\Sigma \log n^a$ , and therefore also  $n_1^{a_1} n_2^{a_2} \dots$  must have a determined value, say

$$n_1^{a_1} n_2^{a_2} \dots = \omega.$$

Herewith the quantity of each constituent is determined. In

fact, let the initial quantities, expressed in gram molecules, be  $\bar{n}_1, \bar{n}_2$ , etc.; these can change into

$$n_1 = \bar{n}_1 + a_1 x, \quad n_2 = \bar{n}_2 + a_2 x, \quad \dots$$

where  $x$ , indicating the progress of the reaction, will be determined by

$$(\bar{n}_1 + a_1 x)^{a_1} (\bar{n}_2 + a_2 x)^{a_2} \dots = \omega.$$

Now, this equation can always be satisfied by one and only one value of  $x$ . In fact, if  $x$  increases, the left-hand member of the equation increases, since such is the case of every factor (whether  $a < 0$  or  $a > 0$ ). Now, if the reaction proceeds from  $\bar{n}_1, \bar{n}_2$ , etc., in the positive direction of  $x$ , in fine, if  $x$  increases from zero, one of the magnitudes  $\bar{n} + ax$ , for which  $a$  is negative, will become zero, *i.e.* one of the gases will entirely disappear. Then the corresponding factor  $(\bar{n} + ax)^a$  will be infinite. Similarly, if  $x$  is allowed to vary in the negative direction, one of the magnitudes  $\bar{n} + ax$  with a positive  $a$  will vanish, and the corresponding factor will be zero. Since thus the left-hand member of the equation mounts from 0 to  $\infty$ , while  $x$  moves always in the same direction, it will once pass through the value  $\omega$ .

If the temperature is kept constant, we have for the determination of the dissociation-equilibrium, in its dependence on volume,

$$\Sigma \log \left( \frac{n}{v} \right)^a = \text{const.}$$

or

$$\left( \frac{n_1}{v} \right)^{a_1} \left( \frac{n_2}{v} \right)^{a_2} \dots = \text{const.} = K, \text{ say.} \quad (66)$$

If  $a_1 + a_2 + \dots = 0$ , that is to say, if the number of molecules is unaltered by the reaction,  $v$  drops out. Then, in an isothermal expansion or contraction, the quantities of the gases do not change. If, however,  $a_1 + a_2 + \dots \neq 0$ , there will be a change. The equilibrium values  $n$  for a single value of  $v$  being known, the formula suffices to calculate them for any other volume. Suppose that  $a_1 + a_2 + \dots > 0$ . Then with increasing volume  $n_1^{a_1} n_2^{a_2} \dots$  will increase, that is to say, the reaction will proceed in such a direction that  $n$  will increase for the gases with a positive  $a$ , and decrease for the remaining ones. Whence it can readily be concluded that the total number of molecules will increase.

Let 1, 2, etc., be the gases for which  $\alpha$  is positive, and 1', 2', etc., those for which  $\alpha$  is negative, say  $= -\beta$ . Then the reaction consists in the change of  $\alpha_1, \alpha_2, \dots$  molecules of the former into  $\beta_1, \beta_2, \dots$  molecules of the latter gases, or *vice versa*, and the condition of equilibrium can be written

$$\frac{\left(\frac{n_1}{v}\right)^{\alpha_1} \left(\frac{n_2}{v}\right)^{\alpha_2} \dots}{\left(\frac{n'_1}{v}\right)^{\beta_1} \left(\frac{n'_2}{v}\right)^{\beta_2} \dots} = K.$$

This is Guldberg and Waage's law. The fractions  $\frac{n_1}{v}$ , etc., multiplied by one and the same constant, represent the numbers of molecules per unit volume. If the reaction is to take place in one direction,  $\alpha_1, \alpha_2, \dots$  molecules of the first group of gases must come together under favourable conditions. The number of times this happens per second is proportional to  $\left(\frac{n_1}{v}\right)^{\alpha_1} \left(\frac{n_2}{v}\right)^{\alpha_2} \dots$

Similarly, the number of times that  $\beta_1, \beta_2, \dots$  molecules of the second group of gases come together, so that the inverse reaction may take place, is proportional to  $\left(\frac{n'_1}{v}\right)^{\beta_1} \left(\frac{n'_2}{v}\right)^{\beta_2} \dots$

Whence the law of equilibrium. (*Note*.—If one of the groups consists only of a single gas for which  $\alpha$ , or  $\beta$ , has the value 1, there is no question of the meeting of two or more molecules; but even then one gets the above law, viz. by assuming that within a time interval a certain fraction of the molecules are being dissociated. This, however, is not free from objections. Cf. J. Perrin, *Annales de physique* (9), vol. xi., 1919, p. 1.)

By (66) and (65),

$$\log K = \frac{1}{R} \sum \alpha \left( s - \frac{u}{T} \right) - \sum \alpha. \quad (67)$$

The coefficient  $K$  has at a given temperature a determined value which is independent of the quantities of the gases put together. We now ask how this coefficient depends on temperature.

By the last formula we have

$$\frac{d \log K}{dT} = \frac{1}{R} \sum \alpha \left( \frac{\partial s}{\partial T} - \frac{1}{T} \frac{\partial u}{\partial T} + \frac{u}{T^2} \right)$$

or, since for each gas

$$\frac{\partial s}{\partial T} = \frac{1}{T} \frac{\partial u}{\partial T},$$

$$\frac{d \log K}{dT} = \frac{1}{RT^2} \Sigma au.$$

We say that a reaction takes place in the "positive" direction, if the  $n$ 's for gases with positive  $a$ 's increase. Thus, in a positive displacement of equilibrium  $K$  increases. Now, in a positive reaction of amount 1 (at constant temperature) the change of the numbers of gram molecules is represented by  $a_1, a_2$ , etc., so that the change of energy is  $\Sigma au$ , and the heat of reaction,

$$Q = -\Sigma au. \quad . \quad . \quad . \quad . \quad (68)$$

We have therefore (van 't Hoff)

$$\frac{d \log K}{dT} = -\frac{Q}{RT^2},$$

whence we see that if in a positive reaction (at constant temperature) heat is generated ( $Q > 0$ ), then a temperature rise displaces the equilibrium in the negative direction. This is connected with the stability of the equilibrium.

### 30. NERNST'S DETERMINATION OF GAS EQUILIBRIA FROM PURELY THERMODYNAMICAL DATA

Thus far we have spoken of the effect of a volume or temperature variation upon the equilibrium. If we wish to calculate for a given  $T$  the value of  $\log K$  itself, then the chemical constant comes into play. In fact,

$$\frac{\partial s}{\partial T} = \frac{c_v}{T},$$

and we can put

$$S = \int_{T_0}^T \frac{c_v}{T} dT + a, \quad . \quad . \quad . \quad . \quad (69)$$

where  $a$  will now be what we shall call the chemical constant of the gas. Notice that  $a$  for a monatomic gas differs by a certain constant term from the previous  $a$  which we will

now denote by  $\bar{a}$ . In fact, for a monatomic gas we have according to the previous formula, for  $v=1$ , per gram molecule,

$$s = \frac{3}{2}R \log \left( \frac{3}{2}RT \right) + \bar{a},$$

while by what has just been said and remembering that  $c_v = \frac{3}{2}R$ , and putting  $T_0 = 1$ ,

$$s = \frac{3}{2}R \log T + a,$$

so that

$$a = \bar{a} + \frac{3}{2}R \log \left( \frac{3}{2}R \right).$$

By (68) and (69), formula (67) becomes

$$\log K = \frac{1}{R} \Sigma a \int_{T_0}^T \frac{c_v}{T} dT + \frac{Q}{RT} - \Sigma a + \frac{1}{R} \Sigma aa.$$

Now,

$$\frac{dQ}{dT} = -\Sigma a \frac{\partial u}{\partial T} = -\Sigma a c_v,$$

and if to  $T_0$  corresponds  $Q_0$ ,

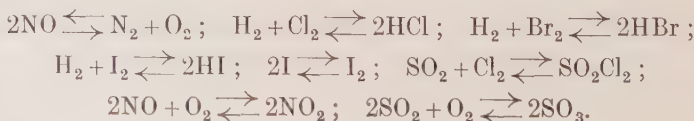
$$Q = Q_0 - \Sigma a \int_{T_0}^T c_v dT.$$

The formula for  $\log K$  can therefore be written

$$\log K = \frac{1}{R} \Sigma a \left[ \int_{T_0}^T \frac{c_v}{T} dT - \frac{1}{T} \int_{T_0}^T c_v dT \right] + \frac{Q_0}{RT} - \Sigma a + \frac{1}{R} \Sigma aa.$$

Thus, if we know the heat of reaction  $Q_0$  for a single temperature, further, the specific heats  $c_v$  for all temperatures, and the chemical constants  $a$  of the gases, we can completely determine the equilibrium for every temperature.

This is Nernst's famous determination of the gas equilibria from purely thermodynamical data. It is applied in various papers by Nernst and in Pollitzer's book to numerous special cases. In these applications the chemical constants are chosen, as far as possible, empirically, *e.g.* by deriving them from observed vapour pressures. Recently, Cederberg has calculated afresh many equilibria, using for the chemical constants values furnished by the logarithm of the critical pressure. He treats the following reactions :





But we shall not enter upon this any further, since for us the principal question is, whether the chemical constants can be derived from the theory of quanta. As regards this, we cannot say much, since for that purpose we would have to be able to apply the theory to polyatomic gases. The question arises also whether it is legitimate to apply, without further investigation, Gibbs' theorem on the entropy of a gas mixture. With regard to all this we are still in the dark. We can explain, however, to a certain extent the appearance of the chemical constants in the formula for  $\log K$ . In fact, suppose that in some way or other the number of elementary states, of which one of the gases with given energy is capable, increases. This will raise the entropy constant of that gas and displace the equilibrium in such a way that there will be more of that gas. In fact, if the number of elementary states by which a certain macroscopic state of a gas can be realised is great, then a great quantity of just *that* gas will favour the number of ways in which a certain macroscopic state of the whole system can be brought about.

Now, the formula for  $\log K$  shows indeed that when the chemical constant of one of the gases, say  $G$ , is increased, the equilibrium of the system is displaced in such a way that we get more of that gas. For, if the gas  $G$  belongs to the first group, with positive  $a$ 's, then an increase of its chemical constant  $a$  increases the sum  $\Sigma aa$ , and therefore the value of  $\log K$ . The equilibrium is displaced in the positive direction, so that the quantity of  $G$  becomes greater. If, on the other hand, the gas  $G$  belongs to the second group, then an increase of its chemical constant leads to a decrease of  $\Sigma aa$ ;  $\log K$  becomes smaller, the equilibrium is displaced in the negative direction, and the quantity of  $G$  again increases.

Something similar holds for the vapour pressure. When the chemical constant  $a$  increases, so also does  $\log p$ , and if the system is contained in a closed space, the amount of vapour will increase. The effect of the chemical constant  $a$  is, relatively, the smaller the higher the temperature. This is readily seen in the case of the vapour pressure at least.

### 31. REMARK ON GULDBERG AND WAAGE'S LAW

This law implies the following property. A gas mixture subjected to gravity is in dissociation equilibrium at every level,

if each gas expands in its own way over the available space. In fact, if the  $z$ -axis be directed vertically upwards, the condition of equilibrium is

$$\frac{dp}{dz} = -g\rho m,$$

where  $\rho$  is the density expressed in gram molecules per unit volume. But  $p = RT\rho$ , and therefore,

$$\frac{d\rho}{dz} = -\frac{gm}{RT}\rho,$$

$$\rho = \rho_0 e^{-\frac{gm}{RT}z}.$$

By Guldberg and Waage's law [Art. 29],

$$K = \frac{\rho_1^{\alpha_1} \rho_2^{\alpha_2} \dots}{\rho'_1 \beta_1 \rho'_2 \beta_2 \dots},$$

and this must have, at constant  $T$ , a determined value. Now, this can be satisfied for all levels at the same time. For, if we substitute in  $K$  the value just found for  $\rho$ , the numerator becomes, apart from a constant factor,

$$e^{-\frac{gz}{RT}(m_1\alpha_1 + m_2\alpha_2 + \dots)},$$

and the denominator,

$$e^{-\frac{gz}{RT}(m'_1\beta_1 + m'_2\beta_2 + \dots)},$$

and these expressions are equal to each other, since, by the reaction formula,

$$m_1\alpha_1 + m_2\alpha_2 + \dots = m'_1\beta_1 + m'_2\beta_2 + \dots$$

### 32. SPINNING MOTION OF A MOLECULE

We will now apply the theory of quanta to the spinning motion of a molecule, as has been done by Einstein and Stern, Ehrenfest, Schwarzschild, Planck, and Epstein. This application is of importance in connection with the specific heat of a gas at low temperatures, especially of hydrogen, and with the absorption and emission in the infra-red. For a first discussion we treat the molecule as a rigid body and we begin by investigating its permitted or possible modes of motion.

Let us first consider the general case, in which the three principal moments of inertia are all different.

We know that the motion of a rigid body [under no forces]

consists in the rolling of its ellipsoid of inertia on a fixed plane,\* the invariable plane, or also of a cone attached to the body on a cone fixed in space (Poinsot's motion). The perpendicular drawn from the centre of the body upon the invariable plane coincides in direction with the resulting moment of momentum.

But, for the present, it will be more convenient to treat the problem analytically, not geometrically.

Let  $OX$ ,  $OY$ ,  $OZ$  be the principal axes and  $I$ ,  $K$ ,  $L$  the corresponding principal moments of inertia of the body.

The orientation of the body can be determined by three angles.

Imagine a sphere, say of radius 1, drawn around the centre of gravity. Let the positive sense of a rotation about a point of this spherical surface be that which seen from outside appears counter-clockwise. Let the rotation about  $OX$  which carries  $OY$  into  $OZ$  be positive.

Let  $OA$  (Fig. 6) be a fixed line in space, and  $OAB$  a fixed plane through it. In the first place, we can fix the position of  $OZ$  by the angles  $\psi$  and  $\theta$  shown in the figure. Thus an increase of  $\psi$  will correspond to a positive rotation about  $OA$ .

If we move along the great circle  $AZ$  through a quadrant, we arrive at a certain point  $X'$ , and we can always so place the body that its first principal axis of inertia shall fall along  $OX'$ . Then its second axis will have a determined position  $OY'$ . Increasing  $\theta$  will correspond to a positive rotation about  $OY'$ .

The actual position can now be obtained from the position  $OX'$ ,  $OY'$ ,  $OZ$  by a rotation  $\phi$  about  $OZ$ . Manifestly,  $X'X = Y'Y = \phi$ .

The angles which  $OA$  makes with the axes  $OX$ ,  $OY$ ,  $OZ$  will be given by

$$\cos AZ = \cos \theta,$$

$$\cos AY = \sin AZ \cos AYZ = \sin \theta \sin \phi,$$

$$\cos AX = \sin AZ \cos AZX = -\sin \theta \cos \phi.$$

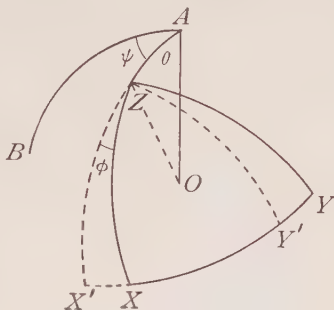


FIG. 6.

\* [With its centre fixed.]

Now for the angular velocities. If of the angles only  $\psi$  changes, we have an angular velocity  $\dot{\psi}$  about  $OA$ ; this can be resolved into the angular velocities  $-\dot{\psi} \sin \theta \cos \phi$ ,  $\dot{\psi} \sin \theta \sin \phi$ ,  $\dot{\psi} \cos \theta$  about  $OX$ ,  $OY$ ,  $OZ$  respectively. If  $\theta$  alone varies, we have an angular velocity  $\dot{\theta}$  about  $OY'$ , and this gives a component  $\dot{\theta} \cos \phi$  about  $OY$  and a component  $\dot{\theta} \sin \phi$  about  $OX$ . Finally, to the change of  $\phi$  corresponds an angular velocity  $\dot{\phi}$  about  $OZ$ . Thus, the total angular velocities about  $OX$ ,  $OY$ ,  $OZ$  are

$$\begin{aligned} & -\dot{\psi} \sin \theta \cos \phi + \dot{\theta} \sin \phi, \\ & \dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi, \\ & \dot{\psi} \cos \theta + \dot{\phi}. \end{aligned}$$

Whence, the components along  $OX$ ,  $OY$ ,  $OZ$  of the moment of momentum,

$$\begin{aligned} p_x &= I(-\dot{\psi} \sin \theta \cos \phi + \dot{\theta} \sin \phi), \\ p_y &= K(\dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi), \\ p_z &= L(\dot{\psi} \cos \theta + \dot{\phi}), \end{aligned}$$

and the kinetic energy,

$$\begin{aligned} T &= \frac{1}{2}I(\dot{\theta} \sin \phi - \dot{\psi} \sin \theta \cos \phi)^2 + \frac{1}{2}K(\dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi)^2 \\ &\quad + \frac{1}{2}L(\dot{\psi} \cos \theta + \dot{\phi})^2. \end{aligned}$$

### 33. INTRODUCTION OF HAMILTON-JACOBI'S PARTIAL DIFFERENTIAL EQUATION. QUANTUM CONDITIONS

We determine a motion by the initial and the final states and by the energy, for which we can now take  $T$ . The energy and the initial co-ordinates being considered as given, the action  $W$  is a function of the end co-ordinates  $\psi$ ,  $\theta$ ,  $\phi$ , and we have

$$\frac{\partial W}{\partial \psi} = p_\psi, \quad \frac{\partial W}{\partial \theta} = p_\theta, \quad \frac{\partial W}{\partial \phi} = p_\phi.$$

From the formula for  $T$  follows

$$\begin{aligned} p_\psi &= \frac{\partial T}{\partial \dot{\psi}} = I(\dot{\psi} \sin \theta \cos \phi - \dot{\theta} \sin \phi) \sin \theta \cos \phi \\ &\quad + K(\dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi) \sin \theta \sin \phi + L(\dot{\psi} \cos \theta + \dot{\phi}) \cos \theta, \\ p_\theta &= \frac{\partial T}{\partial \dot{\theta}} = I(\dot{\theta} \sin \phi - \dot{\psi} \sin \theta \cos \phi) \sin \phi \\ &\quad + K(\dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi) \cos \phi, \\ p_\phi &= \frac{\partial T}{\partial \dot{\phi}} = L(\dot{\psi} \cos \theta + \dot{\phi}) \end{aligned}$$

whence

$$I(\dot{\theta} \sin \phi - \dot{\psi} \sin \theta \cos \phi) = -p_{\psi} \frac{\cos \phi}{\sin \theta} + p_{\theta} \sin \phi + p_{\phi} \cot \theta \cos \phi,$$

$$K(\dot{\psi} \sin \theta \sin \phi + \dot{\theta} \cos \phi) = p_{\psi} \frac{\sin \phi}{\sin \theta} + p_{\theta} \cos \phi - p_{\phi} \cot \theta \sin \phi,$$

and finally,

$$\frac{1}{I} \left\{ p_{\psi} \frac{\cos \phi}{\sin \theta} - p_{\theta} \sin \phi - p_{\phi} \cot \theta \cos \phi \right\}^2 + \frac{1}{K} \left\{ p_{\psi} \frac{\sin \phi}{\sin \theta} + p_{\theta} \cos \phi - p_{\phi} \cot \theta \sin \phi \right\}^2 + \frac{1}{L} p_{\phi}^2 = 2T. \quad (70')$$

Replacing here  $p_{\psi}$ ,  $p_{\theta}$ ,  $p_{\phi}$  by  $\frac{\partial W}{\partial \psi}$ ,  $\frac{\partial W}{\partial \theta}$ ,  $\frac{\partial W}{\partial \phi}$  we get the required differential equation. But the variables cannot be separated. In spite of this, as was shown by Epstein, we can quantise.

We have

$$p_{\psi} = -p_x \sin \theta \cos \phi + p_y \sin \theta \sin \phi + p_z \cos \theta,$$

$$p_{\theta} = p_x \sin \phi + p_y \cos \phi,$$

$$p_{\phi} = p_z.$$

From the first of these equations we see that

$$p_{\psi} = p_a,$$

where  $p_a$  is the component of the moment of momentum along the fixed direction  $OA$ .

The first equation of motion is

$$p_{\psi} = C,$$

so that  $p_a = C$ , which is also obvious.

Let us now assume, after Epstein, that  $OA$  is the direction of the resulting moment of momentum, so that the latter will have the value  $C$ . Then

$$p_x = -C \sin \theta \cos \phi, \quad p_y = C \sin \theta \sin \phi, \quad p_z = C \cos \theta,$$

and therefore,

$$p_{\psi} = C, \quad p_{\theta} = 0, \quad p_{\phi} = C \cos \theta.$$

With these values equation (70') becomes

$$\left( \frac{\cos^2 \phi}{I} + \frac{\sin^2 \phi}{K} \right) \sin^2 \theta + \frac{1}{L} \cos^2 \theta = \frac{2T}{C^2}. \quad (70)$$

We now introduce as quantum conditions

$$\int_0^{2\pi} p_\psi d\psi = n_1 h, \quad \int_0^{2\pi} p_\phi d\phi = n_2 h. \quad . \quad . \quad (71)$$

The first of these gives

$$C = \frac{n_1 h}{2\pi}, \quad . \quad . \quad . \quad . \quad (72)$$

which quantises the resulting moment of momentum.

The second condition can be developed by making use of (70) in order to express  $\cos \theta$  and thus also  $p_\phi$  in terms of  $\phi$ . Put for brevity

$$L\left(\frac{\cos^2 \phi}{I} + \frac{\sin^2 \phi}{K}\right) = a, \quad \frac{2LT}{C^2} = b.$$

Then (70) will be  $\cos^2 \theta + a \sin^2 \theta = b$ , whence

$$p_\phi = C \cos \theta = C \sqrt{\frac{b-a}{1-a}}.$$

Thus the second of (71) will become, in virtue of (72),

$$\int_0^{2\pi} \sqrt{\frac{2T/C^2 - (\cos^2 \phi/I + \sin^2 \phi/K)}{1/L - (\cos^2 \phi/I + \sin^2 \phi/K)}} d\phi = 2\pi \frac{n_2}{n_1}. \quad . \quad (73)$$

### 34. DISCUSSION

From what precedes it appears that for a [rigid] rotating molecule we can have two quantum conditions only. We may note in this connection that Epstein, in one of his various considerations, introduces three such conditions. He chooses, in fact, three fixed axes with which the moving principal axes of the molecule coincide at a certain instant. If  $p_x, p_y, p_z$  be the moments of momentum with respect to these fixed axes (which are constant magnitudes), he puts

$$p_x = \frac{n_1 h}{2\pi}, \quad p_y = \frac{n_2 h}{2\pi}, \quad p_z = \frac{n_3 h}{2\pi}. \quad . \quad . \quad (74)$$

This, however, seems doubtful, because these three conditions are not such as to enable us to say whether a given motion of the molecule is permitted or not. For in the course of the motion the principal axes assume all kinds of orientation. One of these has to be picked out as the orientation of the fixed axes, and the choice is not irrelevant. For if the conditions (74) are satisfied



with one choice, they will not be so with another. We are thus unable to say whether a certain motion is permitted or not, since we have nothing to base the choice upon.

Let us, therefore, return to the two quantum conditions deduced in Art. 33, which also are borrowed from Epstein. For their discussion it is desirable to use Poinso't's geometrical representation of the motion.

The principal moments of inertia being again  $I$ ,  $K$ ,  $L$ , the equation of the ellipsoid of inertia is

$$Ix^2 + Ky^2 + Lz^2 = 1,$$

so that its semi-axes are

$$\frac{1}{\sqrt{I}}, \quad \frac{1}{\sqrt{K}}, \quad \frac{1}{\sqrt{L}}.$$

We will henceforth refer everything to the axes  $OX$ ,  $OY$ ,  $OZ$ .

Let  $x$ ,  $y$ ,  $z$  be the co-ordinates of the point of contact of the ellipsoid with the invariable plane. Then the direction cosines of the normal to the plane are proportional to  $Ix$ ,  $Ky$ ,  $Lz$  and thus also to the components of the moment of momentum, since  $x$ ,  $y$ ,  $z$  are proportional to the components  $q_x$ ,  $q_y$ ,  $q_z$  of the angular velocity.

The perpendicular  $\delta$  from the centre on the plane is given by

$$\delta^2 = \frac{1}{I^2x^2 + K^2y^2 + L^2z^2}.$$

Now, if the angular velocity is

$$q_x = \lambda x, \quad q_y = \lambda y, \quad q_z = \lambda z,$$

then

$$2T = \lambda^2(Ix^2 + Ky^2 + Lz^2) = \lambda^2$$

and, the resulting moment of momentum,

$$C^2 = \lambda^2(I^2x^2 + K^2y^2 + L^2z^2),$$

so that

$$\delta^2 = \frac{2T}{C^2}. \quad . \quad . \quad . \quad . \quad . \quad (75)$$

Thus  $\delta$  has, for each Poinso't-motion, some constant value which lies, of course, between the greatest and the smallest semi-axis of the ellipsoid. The motion can be characterised by drawing upon the surface of the ellipsoid a line, at whose points the tangential plane has the constant distance  $\delta$  from the centre.

This is the polhode. The different polhodes fall into two groups. Let  $OA, OB, OC$  (Fig. 7) be the semi-axes in the order of decreasing

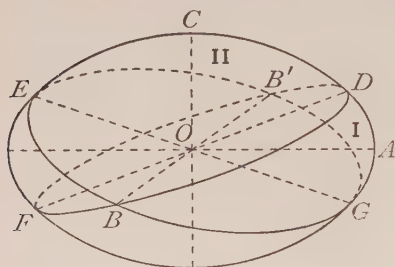


FIG. 7.

length, and  $D, E, F$  the points of the ellipse  $AC$  where the tangential plane has the distance  $OB$  from the centre  $O$ . Lay a plane through  $DF$  and  $OB$ , and another plane through  $EG$  and  $OB$ . The surface of the ellipsoid will thus be divided into four regions.

The polhodes in region I form closed curves round  $A$  which at first are small ellipses and then approach  $DBGB'$ . In a similar way the polhodes of region II are distributed around  $C$ .

The quantum conditions can now be written :

$$2\pi C = n_1 h$$

and

$$C \int_0^{2\pi} \cos \theta d\phi = C \int_0^{2\pi} \sqrt{\frac{b-a}{1-a}} d\phi = n_2 h,$$

i.e.

$$C \int_0^{2\pi} \sqrt{\frac{L\delta^2 - L(\cos^2 \phi/I + \sin^2 \phi/K)}{1 - L(\cos^2 \phi/I + \sin^2 \phi/K)}} d\phi = n_2 h,$$

$a$  being as before and

$$b = \frac{2LT}{C^2} = L\delta^2.$$

In Fig. 6,  $\theta$  is the angle which the axis  $OZ$  makes with the normal on the invariable plane. It will be seen from this figure that  $\theta$  and  $\pi - \phi$  are the spherical polar co-ordinates of the normal with respect to  $OZ$ . Now, since in (71)  $\phi$  is expressly assumed to extend over the interval 0 to  $2\pi$ , the quantum conditions can be applied only to motions in which the polhode goes round  $OZ$ . Consequently we must take for  $OZ$  the axis of greatest or smallest moment of inertia. This follows also at once from the formulae.

The various motions can be classified according to the value of  $b$ .

If  $b = 1$ , then  $\theta = 0$ ,  $\delta^2 = 1/L$ . This gives a permanent rotation about a principal axis. Now, for  $OZ$  any principal axis can be taken, so that we have three kinds of motion, unless we feel inclined to exclude that about the mean axis as unstable.

If  $b$  differs from 1, then  $a$  must nowhere in the interval  $\phi=0$  to  $2\pi$  become equal to 1. Moreover, we must have  $|b-a| < |1-a|$ . This gives two possibilities, viz.  $a < b < 1$  and  $a > b > 1$ .

1. In the former case  $a < 1$  for every  $\phi$ , so that  $L/I < 1$ ,  $L/K < 1$ . Thus  $L$  must be the smallest moment of inertia and the polhode lies around the point  $A$  of the ellipsoid. In fact (owing to  $a < b < 1$ ) we must have

$$\delta^2 < \frac{1}{L} \text{ and } \delta^2 > \frac{\cos^2 \phi}{I} + \frac{\sin^2 \phi}{K}; \quad \therefore \delta^2 > \frac{1}{I} \text{ and } > \frac{1}{K},$$

that is to say,  $\delta$  must lie between the greatest and the mean semi-axis. If  $n_1$  and  $n_2$  are chosen,  $\delta$  will be determined from the equation

$$\int_0^{2\pi} \sqrt{\frac{L\delta^2 - L(\cos^2 \phi/I + \sin^2 \phi/K)}{1 - L(\cos^2 \phi/I + \sin^2 \phi/K)}} d\phi = 2\pi \frac{n_2}{n_1}. \quad (\text{A})$$

(Of course,  $n_2 < n_1$ .) The angular velocity and thus also the kinetic energy will then be fixed by  $C = n_1 h/2\pi$ . Not every polhode is permitted; the molecule cannot, in general, rotate about an arbitrarily chosen axis. For a small value of  $n_1$  there is only a limited number of possible motions. ✕

The separating polhode [ $DBGB'$ , Fig. 7] is, as a rule, not possible. For, the second quantum condition (with  $I$  as the mean moment of inertia, and  $\delta^2 = 1/I$ ) then becomes

$$2\sqrt{\frac{L}{I} - \frac{\bar{L}}{K}} \int_0^\pi \frac{\sin \phi d\phi}{\sqrt{1 - L(\cos^2 \phi/I + \sin^2 \phi/K)}} = 2\pi \frac{n_2}{n_1},$$

or, with  $\cos \phi = u$ ,

$$\sqrt{\frac{L}{I} - \frac{\bar{L}}{K}} \int_{-1}^{+1} \frac{du}{\sqrt{1 - \frac{L}{I}u^2 - \frac{\bar{L}}{K}(1-u^2)}} = \frac{n_2}{n_1}\pi,$$

$$\text{i.e.} \quad 2 \arcsin \sqrt{\frac{1/I - 1/\bar{K}}{1/L - 1/\bar{K}}} = \frac{n_2}{n_1}\pi,$$

which, as a rule, cannot be satisfied.

If  $\delta^2 > 1/I$ , then a lower limit can be assigned to  $n_2$ . In fact, by (A),

$$2\pi \frac{n_2}{n_1} > 2\sqrt{\frac{L}{I} - \frac{\bar{L}}{K}} \int_0^\pi \frac{\sin \phi d\phi}{\sqrt{1 - L(\cos^2 \phi/I + \sin^2 \phi/K)}}$$

$$\text{or} \quad \pi \frac{n_2}{n_1} > 2 \arcsin \sqrt{\frac{1/I - 1/\bar{K}}{1/L - 1/\bar{K}}}.$$

If  $I$  differs very little from  $L$ , the second member of this inequality can so closely approach  $\pi$  that there will be no integer  $n_2$  (which must be smaller than  $n_1$ ) satisfying it. In this case the region I is very narrow.

II. Similar considerations hold for the case  $a > 1$ . We then have  $L/I > 1$ ,  $L/K > 1$ , so that  $L$  must be the greatest moment of inertia. We have in this case to do with polhodes surrounding another pole.

The values of  $C$  and  $\delta$ , and thus also that of  $T$ , are again determined by  $n_1$  and  $n_2$ .

### 35. TWO EQUAL MOMENTS OF INERTIA

We can now readily pass to the case of two equal moments of inertia. In this case we have to do with an ellipsoid of revolution. One of the regions I and II (Fig. 7) drops out. The polhodes become circles. The axis of symmetry of the molecule is that of the least or the greatest moment of inertia.

Let us put  $I = K$ . Then the second quantum condition (73) will become

$$\frac{L\delta^2 - L/I}{1 - L/I} = \frac{n_2^2}{n_1^2}. \quad (76)$$

If  $L$  be the least moment of inertia, we must have

$$L\delta^2 > \frac{L}{I}, \quad \text{i.e. } \delta^2 > \frac{1}{I}.$$

$$\delta^2 = \frac{1}{I} \text{ is attained for } n_2 = 0.$$

From (75), (72), and (76) follows

$$T = \frac{h^2}{8\pi^2} \left\{ \frac{n_2^2}{L} + \frac{n_1^2 - n_2^2}{I} \right\},$$

agreeing with Schwarzschild's result.

### 36. MOLECULES SPINNING ABOUT A FIXED AXIS

Ehrenfest has considered the case of molecules which can spin about a fixed axis and obtained good results concerning the specific heat. He assumes that only such motions are possible for which the kinetic energy is a multiple of  $\frac{1}{2}h\nu$ , where  $\nu$  is the

number of revolutions per second, or  $2\pi\nu$  the angular velocity. Thus, if  $I$  be the moment of inertia,

$$\frac{1}{2}I(2\pi\nu)^2 = n \cdot \frac{1}{2}h\nu$$

or

$$\nu = n \frac{h}{4\pi^2 I}$$

The same result is arrived at if we assume that the moment of momentum is always a multiple of  $h/2\pi$ . In fact, this gives  $I \cdot 2\pi\nu = nh/2\pi$  or  $\nu = nh/4\pi^2 I$ , as above.

### 37. SCHWARZSCHILD'S FORMULA APPLIED TO BOHR'S MODEL

Epstein has applied Schwarzschild's formula to Bohr's model of the hydrogen molecule, viz. two equal positive nuclei  $P$  and  $Q$  and two electrons diametrically opposed to each other and revolving in a circle with  $PQ$  as axis and the mid-point of  $PQ$  as centre.

Let us first notice that in the case of a body with two equal moments of inertia the quantum conditions can be given a simple form. Let  $L$  be the moment of inertia with respect to the axis of symmetry  $OZ$ , and  $I$  that with respect to  $OY$  and  $OX$ . The motion can at any instant be resolved into a spin about  $OZ$  and one about an axis perpendicular to  $OZ$ . If to these spins belong the moments of momentum  $p_1$  and  $p_2$ , then we have to put in our previous formulae

$$C^2 = p_1^2 + p_2^2$$

and

$$\cos \theta = \frac{p_1}{C}.$$

Thus the conditions

$$C = n_1 \frac{h}{2\pi} \text{ and } \cos \theta = \frac{n_2}{n_1}$$

give

$$p_1^2 + p_2^2 = \frac{n_1^2 h^2}{4\pi^2}, \quad p_1 = \frac{n_2 h}{2\pi}$$

or

$$p_1 = \frac{n_2 h}{2\pi}, \quad p_2^2 = (n_1^2 - n_2^2) \frac{h^2}{4\pi^2}.$$

These conditions can now be applied to Bohr's model of the hydrogen molecule. The first formula is a direct consequence of the rule by which Bohr determines the possible circular motions of the electrons. In fact, according to this rule the

moment of momentum of each electron with respect to the axis of the molecule must be a multiple of  $h/2\pi$ , and this agrees with the above formula, provided that  $n_2$  is an integer.

The second formula, which can be written

$$q_2^2 = \frac{1}{I^2} (n_1^2 - n_2^2) \frac{h^2}{4\pi^2},$$

determines the possible angular velocities about an axis perpendicular to the join of the positive nuclei.

Now, Epstein supposes that all this can indeed be applied to Bohr's hydrogen molecule, which, however, is somewhat doubtful. He writes  $m$  for the mass of each electron,  $M$  for that of each positive nucleus, further,  $a$  for the radius of the circular orbit and  $2b$  for the distance between the nuclei, and puts for the moments of inertia

$$I = 2Mb^2, \quad L = 2ma^2.$$

(In the first of these formulae the contribution of the electrons to the moment of inertia is neglected.)

Further, Epstein assumes that the lengths  $a$  and  $b$  are such as in Bohr's theory, *i.e.* dependent on  $n_2$ . In this way he is able ultimately to express the kinetic energy in terms of  $n_1$  and  $n_2$ ; similarly the potential energy which depends on  $a$  and  $b$ . But we will not enter upon this subject.

### 38. SPECIFIC HEAT

We will now show in a general way how from similar considerations the value of the specific heat can be inferred. Suppose that a molecule is capable of  $k$  states with regard to its rotation and of  $k'$  states with regard to its translation. The latter are represented in the velocity-space by equal volume elements. We will now determine by a lottery how many out of a total of  $n$  molecules will be in the former and how many in the latter states. Let these numbers be denoted by  $n_1 \dots n_k$  and  $n'_1 \dots n'_{k'}$  respectively. Both the rotation and the translation states of each molecule are to be decided by the lottery. We suppose the  $k'$  translation states to be equally likely, while the probabilities  $w_1 \dots w_k$  of the  $k$  rotation states may differ from each other. The probability that  $n_1$  assigned molecules shall be in the first rotation state is  $w_1^{n_1}$ , and similarly for the



remaining states. Hence, the probability that  $n_1 \dots n'_{k'}$  molecules, no matter which, shall assume the aforesaid states,

$$\frac{n! \, n!}{n_1! \dots n_k! \, n'_1! \dots n'_{k'}!} w_1^{n_1} \dots w_k^{n_k} \left(\frac{1}{k'}\right)^n. \quad (77)$$

We now require that, for a given energy  $\epsilon$ , this probability shall be a maximum. Let  $\epsilon_1 \dots \epsilon_k, \epsilon'_1 \dots \epsilon'_{k'}$  be the energies corresponding to the various states. Then we have to find the values of  $n_1 \dots n_k, n'_1 \dots n'_{k'}$  which satisfy the conditions

$$n_1 + \dots + n_k = n, \quad n'_1 + \dots + n'_{k'} = n,$$

$$n_1 \epsilon_1 + \dots + n_k \epsilon_k + n'_1 \epsilon'_1 + \dots + n'_{k'} \epsilon'_{k'} = \epsilon$$

and for which (77) becomes a maximum.

Replace  $n_1!$ , etc., by  $n_1^{n_1}$ , etc. Then

$$\left(\frac{n_1}{w_1}\right)^{n_1} \dots \left(\frac{n_k}{w_k}\right)^{n_k} n'_1 \epsilon'_1 \dots n'_{k'} \epsilon'_{k'}$$

and therefore also

$$H = n_1 \log \left(\frac{n_1}{w_1}\right) + \dots + n_k \log \left(\frac{n_k}{w_k}\right) + n'_1 \log n'_1 + \dots + n'_{k'} \log n'_{k'}$$

will have to be made a minimum. This, together with the conditions

$$\delta n_1 + \dots + \delta n_k = 0,$$

$$\delta n'_1 + \dots + \delta n'_{k'} = 0,$$

$$\epsilon_1 \delta n_1 + \dots + \epsilon_k \delta n_k + \epsilon'_1 \delta n'_1 + \dots + \epsilon'_{k'} \delta n'_{k'} = 0,$$

gives

$$\log \left(\frac{n_1}{w_1}\right) \delta n_1 + \dots + \log \left(\frac{n_k}{w_k}\right) \delta n_k + \log n'_1 \delta n'_1 + \dots + \log n'_{k'} \delta n'_{k'} = 0.$$

Thus,

$$n_k = C w_k e^{-l \epsilon_k}, \quad n'_{k'} = C' e^{-l \epsilon'_{k'}}.$$

The mean energy of translational motion is  $3/2l$  or also  $\frac{3}{2} kT$ .\* Consequently,  $1/l = kT$  and

$$n_k = C w_k e^{-\frac{\epsilon_k}{kT}}.$$

Hence, the mean energy of the spinning motion,

$$\bar{\epsilon}_r = \frac{\sum \epsilon_k w_k e^{-\frac{\epsilon_k}{kT}}}{\sum w_k e^{-\frac{\epsilon_k}{kT}}}, \quad . \quad . \quad . \quad . \quad (78)$$

---

\* Here  $k$  stands for Planck's constant and will not be confounded with the suffix of a group.

and the contribution of this energy to the specific heat, per molecule,

$$c_r = \frac{1}{(\sum w_k e^{-\frac{\epsilon_k}{kT}})^2} \left\{ \sum \frac{\epsilon_k^2}{kT^2} w_k e^{-\frac{\epsilon_k}{kT}} \cdot \sum w_k e^{-\frac{\epsilon_k}{kT}} - \sum \epsilon_k w_k e^{-\frac{\epsilon_k}{kT}} \cdot \sum \frac{\epsilon_k}{kT^2} w_k e^{-\frac{\epsilon_k}{kT}} \right\}.$$

Let  $a_1, a_2, \dots$  be the values of the various  $\epsilon_k/kT$ . Then

$$\begin{aligned} c_r &= \frac{k\{(a_1^2 w_1 e^{-a_1} + \dots)(w_1 e^{-a_1} + \dots) - (a_1 w_1 e^{-a_1} + \dots)^2\}}{(\sum w_1 e^{-a_1} + w_2 e^{-a_2} + \dots)^2} \\ &= k \frac{\sum(\overline{\mu\nu})(a_\mu - a_\nu)^2 e^{-(a_\mu + a_\nu)} w_\mu w_\nu}{(\sum(\mu) w_\mu e^{-a_\mu})^2}. \end{aligned}$$

Let the smallest of all  $a_\mu$ , say  $a_1$ , be separated by a finite interval from the next one,  $a_2$ . Then, at a sufficiently low temperature,  $e^{-a_2}$ ,  $e^{-a_3}$ , etc., will all be negligible in presence of  $e^{-a_1}$ . Now, since the denominator contains a term with the square of the latter, while this occurs in the numerator only in the first power, multiplied by another  $e^{-a_\mu}$ ,  $c_r$  will tend to zero. It can be shown without trouble that such is also the case of all derivatives of  $c_r$  with respect to  $T$ .

The formulae become somewhat simpler if the probabilities  $w$  are assumed to be all equal. We then have

$$c_r = k \frac{\sum(\overline{\mu\nu})(a_\mu - a_\nu)^2 e^{-(a_\mu + a_\nu)}}{(\sum(\mu) e^{-a_\mu})^2}.$$

For a sufficiently low temperature we can limit ourselves to  $a_1$  and  $a_2$ , so that

$$c_r = k \frac{(a_2 - a_1)^2 e^{-(a_1 + a_2)}}{(e^{-a_1} + e^{-a_2})^2},$$

or approximately, replacing the denominator by  $e^{-2a_1}$ ,

$$c_r = \frac{(\epsilon_2 - \epsilon_1)^2}{kT^2} e^{\frac{\epsilon_1 - \epsilon_2}{kT}}.$$

In the case of spinning about a fixed axis treated by Ehrenfest we have

$$\nu = \frac{n\hbar}{4\pi^2 I}$$

and

$$\epsilon = \frac{1}{2} I (2\pi\nu)^2 = \frac{n^2 \hbar^2}{8\pi^2 I}.$$

From the observed value of  $c_r$  one can calculate  $\epsilon_1 - \epsilon_2$  and thus also the moment of inertia  $I$ . This was actually done, but we shall not dwell upon this subject.

One can require also that a proper result should come out for high temperatures.

Suppose, *e.g.*, that  $\epsilon_\mu = \mu q$  (linear vibrator,  $q$  constant). Then

$$a_\mu = \mu \frac{q}{kT}.$$

By (78), the  $w$ 's being assumed equal,

$$\epsilon_r = kT \frac{\sum a_\mu e^{-a_\mu}}{\sum e^{-a_\mu}}.$$

The denominator is

$$\sum e^{-a_\mu} = \sum e^{-\mu \frac{q}{kT}} = 1 + e^{-\frac{q}{kT}} + e^{-\frac{2q}{kT}} + \dots = \frac{1}{1 - e^{-\frac{q}{kT}}},$$

and the numerator,

$$\sum a_\mu e^{-a_\mu} = \frac{q}{kT} \left\{ e^{-\frac{q}{kT}} + 2e^{-\frac{2q}{kT}} + \dots \right\} = \frac{q}{kT} \frac{e^{-\frac{q}{kT}}}{(1 - e^{-\frac{q}{kT}})^2}.$$

Thus

$$\bar{\epsilon}_r = q \frac{e^{-\frac{q}{kT}}}{1 - e^{-\frac{q}{kT}}},$$

and for high  $T$ ,  $\bar{\epsilon}_r = kT$ .

In Ehrenfest's treatment,  $a_\mu = \mu^2 \frac{h^2}{8\pi^2 I kT}$ , which makes everything somewhat more complicated.

### 39. BJERRUM'S THEORY

Important applications of the theory of spinning molecules to infra-red spectra were made by Bjerrum and Eucken. They concern the absorption lines, especially those produced by water vapour, whose positions were determined by Paschen, Miss E. von Bahr, Rubens, and his pupils. In this work also Langley's older investigations have been utilised. The absorption bands under discussion extend from  $\lambda = 4.7\mu$  to about  $400\mu$ .

We will first consider a beautiful deduction made by Bjerrum. Suppose that a charged particle vibrates along a line  $OL$ , which makes an angle  $\theta$  with the  $x$ -axis and which rotates about this

axis with a constant angular velocity  $\omega$ . Then, if  $a \cos nt$  be the displacement along  $OL$  from the position of equilibrium  $O$ , the co-ordinates of the particle will be

$$a \cos \theta \cos nt, \quad a \sin \theta \cos nt \cos \omega t, \quad a \sin \theta \cos nt \sin \omega t.$$

The last two expressions can be written

$$\frac{1}{2}a \sin \theta [\cos (n + \omega)t + \cos (n - \omega)t]$$

and

$$\frac{1}{2}a \sin \theta [\sin (n + \omega)t - \sin (n - \omega)t],$$

whence we see that, owing to the rotation of the line  $OL$  with the angular velocity  $\omega$ , a vibration of frequency  $n$  is replaced by one of the same frequency and by two others of frequencies  $n + \omega$  and  $n - \omega$ . Thus, if among the molecules occur different angular velocities  $\omega_1, \omega_2$ , etc., we get besides the central line  $n$  a number of other lines  $n \pm \omega_1, n \pm \omega_2$ , etc. Now, the central line of the group under discussion lies at  $\lambda = 6.26$ . The remaining lines lie symmetrically on both sides of it, and if the proposed explanation of their origin is correct, their distances from the central line must be equal when measured in terms of frequency. Thus, if  $\lambda$  and  $\lambda'$  be the wave-lengths of corresponding lines (viz.  $\lambda < 6.26$  and  $\lambda' > 6.26$ ), we must have

$$\frac{1}{\lambda} - \frac{1}{6.26} = \frac{1}{6.26} - \frac{1}{\lambda'}$$

or

$$\frac{6.26\lambda}{6.26 - \lambda} = \frac{6.26\lambda'}{\lambda' - 6.26};$$

in other words, if we calculate

$$\lambda_r = \frac{6.26\lambda}{6.26 - \lambda} \quad \text{and} \quad \lambda'_r = \frac{6.26\lambda'}{6.26 - \lambda'},$$

we must have  $\lambda_r = \lambda'_r$ .

This, of course, is nothing else than a verification of the symmetrical position.  $\lambda_r$  is the wave-length which corresponds to the frequency  $\omega$ , derived from the observed wave-length  $\lambda$ ; similarly,  $\lambda'_r$  is the wave-length corresponding to the same frequency and derived from the observed wave-length  $\lambda'$ .

But the remarkable thing is that the rotation  $\omega$  itself can give rise to an emission and that to such an emission line corresponds also an absorption line. A line of wave-length  $\lambda_r = \lambda'_r$  is actually observed. We can refer to such lines as those of a "rotation spectrum" (whence also the suffix  $r$ ). The rotation lines lie in

the extreme infra-red. In a table given by Rubens and Hettner occur in all 16 lines on the violet side of  $6\cdot26$  and as many corresponding ones on the red side. All these lines were observed by Miss v. Bahr. She saw besides six lines on the violet side, and the corresponding lines on the other side were found by Rubens and Hettner, who discovered also four more lines of great wave-length, lying as far away from  $6\cdot26$  as some lines observed by Langley.

Now, in a dozen or more cases also a rotation line  $\lambda_r$  (of wave-length  $20$  to  $100\mu$ ) was observed.

It will be enough to give here a few examples :

|          |              |       |            |   |          |       |
|----------|--------------|-------|------------|---|----------|-------|
| 1st pair | 5.92, 6.64   | gives | 109, 109   | ; | observed | (106) |
| 2nd      | „ 5.80, 6.78 | „     | 79, 81     | „ | 79       |       |
| 3rd      | „ 5.61, 7.05 | „     | 54, 56     | „ | 58.5     |       |
| 4th      | „ 5.56, 7.17 | „     | 50, 49     | „ | 50       |       |
| 5th      | „ 5.19, 7.88 | „     | 30.3, 31   | „ | 30.8     |       |
| 6th      | „ 5.13, 8.04 | „     | 28.4, 28.2 | „ | 28.8     |       |
| 7th      | „ 4.86, 8.73 | „     | 21.7, 22   | „ | 21.6     |       |

Some of the lines which are here listed as “observed,” viz. the rotation lines, have wave-lengths which bear simple ratios to each other. Thus,  $58\cdot5$ ,  $28\cdot8$ ,  $21\cdot6$  coincide very nearly with  $\frac{1}{3}$ ,  $\frac{1}{6}$ , and  $\frac{1}{8}$  of  $173\cdot4$  (i.e.  $57\cdot8$ ,  $28\cdot9$ , and  $21\cdot7$ ). This agrees with the theory of quanta, if it be assumed that only certain angular velocities occur. In fact, we have found for the frequency  $n\hbar/4\pi^2I$ , so that the frequencies to be expected should bear to each other whole-number ratios. Now, among the observed rotation lines Bjerrum has found seventeen which correspond to  $n=2, \dots 18$ . The constant difference in frequency is

$$\delta\nu = 1\cdot73 \cdot 10^{12},$$

so that

$$\frac{\hbar}{4\pi^2I} = 1\cdot73 \cdot 10^{12},$$

whence the moment of inertia  $I$  can be calculated. One finds  $I=0\cdot22\cdot10^{-39}$ . Since the mass of a molecule of water is  $1\cdot64\cdot10^{-24}$ ,  $18=29\cdot10^{-24}$ , this gives for the radius of gyration

$$\sqrt{\frac{0\cdot22 \cdot 10^{-39}}{29 \cdot 10^{-24}}} = 2\cdot7 \cdot 10^{-9} \text{ cm.},$$

which is a reasonable value.

There is, however, a number of lines (much more than one-half of all) which do not fit into Bjerrum's series. Eucken has shown that these can be ordered into another series, with  $\delta\nu = 0.75 \cdot 10^{12}$ . Some lines, moreover, can be fitted into both series. Thus, for instance, 11.6 falls into Bjerrum's series with  $n = 15$ , and into Eucken's series with  $n = 34$ .

The question arises, therefore, whether two such series can be expected. In the case of three unequal moments of inertia we can have rotations about any of the principal axes of inertia with angular velocities which are multiples of a certain value. Similarly in the case of two equal moments of inertia.

According to the above theory there is still, in the case of unequal moments of inertia, a number of other motions which, however, are not purely periodic. The question is whether these will not outnumber the purely periodic motions. If two of the principal moments of inertia are equal, then all motions which do not consist in a rotation about the axis of symmetry fall into the same series. In fact, if  $I = K \neq L$ , we have always, for the frequency of these motions,  $n_1 h / 4\pi^2 I$ .\* In addition to this there would still be a series with the frequency  $nh / 4\pi^2 L$  produced by rotations about the axis of symmetry. It remains to be seen, however, whether (in view of their relatively rare occurrence) these motions would be efficient enough to be perceptible.

Planck's method of quantising as given in his paper on the structure of the phase-space is somewhat different. According to his view, if  $q_1$  be the angular velocity about the axis of symmetry and  $q_2$  that about a perpendicular axis,

$$q_1 = \frac{nh}{2\pi I} \quad \text{and} \quad q_2 = \frac{n'h}{2\pi I},$$

so that the resultant angular velocity becomes

$$\frac{h}{2\pi} \sqrt{\frac{n'^2}{I^2} + \frac{n^2}{L^2}},$$

---

\* This is the frequency with which the axis of symmetry rotates about the normal of the invariable plane. If  $\alpha$  be the angle between this normal and the equator, then  $C \cos \alpha$  is the moment of momentum about a diameter of the equator and, therefore,  $C \cos \alpha / I$  the angular velocity about that diameter. This can be resolved into a component along the axis of symmetry, which does not affect the position of the latter, and an angular velocity  $C/I$  about the said normal. The corresponding frequency is  $C/2\pi I$  or, by (72),  $n_1 h / 4\pi^2 I$ .



If we put

$$\frac{h}{4\pi^2\bar{L}} = \delta\nu, \quad \frac{h}{4\pi^2\bar{I}} = \delta\nu_1,$$

then the last angular velocity becomes

$$2\pi\sqrt{n^2\delta\nu^2 + n'^2\delta\nu_1^2},$$

so that we could also expect a series with frequencies given by

$$\sqrt{n^2\delta\nu^2 + n'^2\delta\nu_1^2}.$$

We have found before (Art. 37)

$$p_1 = \frac{n_2 h}{2\pi}, \quad p_2^2 = (n_1^2 - n_2^2) \frac{h^2}{4\pi^2},$$

whence

$$q_1 = \frac{n_2 h}{2\pi\bar{L}}, \quad q_2 = \sqrt{n_1^2 - n_2^2} \frac{h}{2\pi\bar{I}}.$$

Thus the relations between  $n_1$ ,  $n_2$  and the numbers  $n$ ,  $n'$  just introduced are

$$n = n_2, \quad n' = \sqrt{n_1^2 - n_2^2}.$$

Planck's resultant moment of momentum is

$$C^2 = (n^2 + n'^2) \frac{h^2}{4\pi^2},$$

so that the frequencies of all motions which do not consist in a rotation about the axis of symmetry are given by

$$\frac{C}{2\pi\bar{I}} = \sqrt{n^2 + n'^2} \cdot \frac{h}{4\pi^2\bar{I}}.$$

This would be the principal series of rotation lines. And another series, with the frequencies

$$\frac{nh}{4\pi^2\bar{L}},$$

would be produced by the rotations about the axis of symmetry.

#### 40. FURTHER REMARKS ON THE MECHANISM OF THESE PHENOMENA

The absorption lines which lie symmetrically on both sides of 6.26 do not offer any difficulties.\* These are encountered,

\* Suppose that the particle considered in Art. 39, which can vibrate with the frequency  $n$  along the spinning line  $OL$ , is subjected to an electric force  $s \cos n't$  along  $OY$ . The component of this force along  $OL$  is

$$s \sin \theta \cos \omega t \cos n't = \frac{1}{2}s \sin \theta \cos (n' + \omega)t + \frac{1}{2}s \sin \theta \cos (n' - \omega)t.$$

There will thus be a strong resonance, if  $n' + \omega = n$  or  $n' - \omega = n$ , that is to say, if  $n' = n - \omega$  or  $n' = n + \omega$ .

however, when one turns to the proper rotation lines. If we first suppose, which no doubt would also be the view of Bjerrum and others, that to these rotation lines correspond also emission lines, we should have to assume that the molecules can emit radiation of just their own allowed frequencies. But this is against Bohr's idea. Besides, one fails to see how the allowed rotatory motion could then persist.

The absorption is not easy to understand. Of an ordinary "resonance" there can be no question. It is difficult to say what happens to a particle which can spin or does already spin and which is exposed to an incident radiation. This question was considered by Planck and, before him, by Fokker, with a view to the theory of radiation. But we shall leave it on one side and shall make only the following remark. It appears that, after all, a rotating particle can really absorb, provided, however, that its angular velocity is changing. This has led Planck to assume that actually all angular velocities and thus also all frequencies  $\omega$  can occur, but that the distribution function  $W(\omega)$  changes discontinuously at the particular values of  $\omega$  which are prescribed by the quantum conditions and remains constant between two such successive values. Now, according to Planck the absorption is proportional to  $-\omega \frac{dW(\omega)}{d\omega}$  and thus differs from zero only at the places of discontinuity. (In reality, however, there is undoubtedly always some absorption.) This conception, according to which all angular velocities would be possible, clashes with the explanation of the lines distributed symmetrically about 6.26.

#### 41. BAND SPECTRA

Suppose that a number of electrons revolve round a molecule which itself can rotate, and let their motion be independent of that of the molecule, and *vice versa*. Let  $E$  be the kinetic energy of the electrons and  $* n^2 h^2 / 8\pi^2 I$  the energy of the molecule.

Then, in passing from one state to another,

$$\nu = \frac{E - E'}{h} + (n^2 - n'^2) \frac{h}{8\pi^2 I}.$$

---

\* Cf. the last formula of Art. 35.

If  $E$ ,  $E'$ , and  $n'$  are kept fixed, then

$$\nu = a + bn^2, \quad b = \frac{h}{8\pi^2 I}.$$

(This is Deslandres' formula which holds, approximately, for many bands.) The band extends from a "head" towards the violet. The reverse extension can also be obtained. From the constant  $b$  the moment of inertia  $I$  can be calculated. Schwarzschild finds for it values which are of the right order.

### THEORY OF ELECTRIC DIPOLES

We will now briefly consider Debye's theory of electric dipoles, although it is not related to the quantum theory. The theory has been developed by Debye with the object of accounting for the variation of the dielectric constant with temperature. So long as the molecules or the atoms are supposed to contain electrons or ions bound quasi-elastically to certain equilibrium positions, no appreciable influence of the temperature can be expected. If we assume, however, the existence of dipoles which have invariable electric moments but which can be turned around in heat motion, then we can understand that their axes will be oriented by an electric field the less the higher the temperature. The case is then much the same as that considered by Langevin in his theory of paramagnetism. Also the results are analogous to those of Langevin (Curie's law).

Following Debye, we will investigate the effect of an alternating field and thence derive some conclusions concerning refraction and absorption in the infra-red. The main point will be that in rapidly alternating electric fields the molecules are oriented to a lesser degree than in a constant field; the electric moment will thus be smaller in amplitude than if the force varied very slowly, and it will besides lag behind the force in phase; on the latter will depend the absorption.

This lag of the rotating molecules, however, must not be associated with the effect of their mass (moment of inertia) which would manifest itself by the appearance in the equation of motion, along with the couple  $K$  acting upon the molecule and with the opposite sign, of the product of the moment of inertia into the angular velocity. The latter term is in reality too small to make

itself perceptible. The theory, as developed by Debye, can be compared with that of Brownian movement and with the explanation of the manner in which the particles distribute themselves in an emulsion subjected to an alternating vertical field of force.

If the emulsion is placed in a constant field of force, such as that of gravity, we have the case of Perrin's experiments. The force of gravity pulls the particles down with a velocity depending on the resistance, while diffusion drives them upwards. The equilibrium between these two actions can be described by saying that through a horizontal plane as many particles pass downwards owing to gravity as go upwards owing to diffusion, or that the changes of the number of particles in a layer of infinitesimal thickness, which would be produced by either cause taken separately, cancel. The diffusion can be considered as a consequence of Brownian movement, and in so far does the latter come into play. The case of a variable vertical field of force can be treated in the same way, with the difference, however, that now the number of particles in a thin layer will not be constant.

Debye's theory follows upon similar lines, only that instead of an infinitely thin layer one has now to consider a cone of aperture  $d\omega$  wherein lie the axes of a number of molecules. The electric force gives to the molecules certain angular velocities, determined by a resistance. Owing to this spinning motion the number of molecules whose axes lie within  $d\omega$  (and which we will briefly call the molecules within  $d\omega$ ) will change. And another cause of such changes is the Brownian movement, *i.e.* the heat rotation of the molecules.

1. Let the electric force  $E$  be constant in direction and intensity. Take its direction  $OP$  as the polar axis and determine the orientation of the moment of a particle (molecule) by the polar co-ordinates  $\theta$  and  $\phi$ . For the sake of simplicity consider the particle as a thin rod with equal and opposite electric charges at its ends. An appreciable kinetic energy will then correspond only to rotations about an axis perpendicular to the rod, *viz.*

$$\frac{1}{2}Q(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta).$$

The potential energy is, apart from an additive constant,  $-Em \cos \theta$ ,  $m$  being the moment of the particle. If  $p_\phi$  and  $p_\theta$  be

the momenta corresponding to  $\phi$  and  $\theta$ , the number of particles in a group is

$$Ce^{-\frac{Q(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) - 2Em \cos \theta}{2kT}} d\theta d\phi dp_\theta dp_\phi,$$

and since

$$p_\theta = Q\dot{\theta}, \quad p_\phi = Q\dot{\phi} \sin^2 \theta,$$

this number can be written

$$C'e^{-\frac{Q(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) - 2Em \cos \theta}{2kT}} \sin^2 \theta d\theta d\phi d\dot{\theta} d\dot{\phi}.$$

Hence, integrating over  $\dot{\theta}$  and  $\dot{\phi}$ , we find, for the number of particles whose axes fall into the interval  $d\theta d\phi$ ,

$$C''e^{\frac{Em \cos \theta}{kT}} \sin \theta d\theta d\phi.$$

Ultimately, therefore, the number of particles which, in the stationary state, lie within the cone  $d\omega$  will be

$$Ce^{\frac{Em \cos \theta}{kT}} d\omega,$$

where  $C$  is some new constant.

2. Let us now consider the Brownian movement during a very short time  $\tau$ . The probability that a particle which initially had the direction  $R$  (this can be marked upon a sphere of radius 1) shall at the end of the time  $\tau$  lie within the element  $d\omega$  at an angular distance  $a$  from  $R$  can, at any rate, be represented by  $f(a)d\omega$ . If it be assumed that  $\tau$  and thus also the implied values of  $a$  are very small, the form of the function  $f$  can be specified. In fact, the motions of the point  $Q$ , which marks upon the unit sphere the direction of the molecule, can then be considered as taking place in a plane and as equally likely to proceed from a given starting-point in all directions, and in the same way for every starting-point. Whence it can be derived that  $f(a) = Ae^{-ha^2}$ , where  $h$  is a constant which will be determined presently.

3. If the electric force oscillates as to its intensity but has always the fixed direction  $OP$ , then the number  $n d\omega$  of particles which lie within the cone  $d\omega$  can only be a function of  $\theta$ . We now consider a given element  $d\omega$  and ask how many particles will lie in it after the time  $\tau$ , if the Brownian movement only is taken into account. A neighbour element  $d\omega'$  contains initially  $n' d\omega'$  particles and of these

$$\frac{h}{\pi} n' e^{-ha^2} d\omega d\omega'$$

fall, at the end of the time  $\tau$ , into  $d\omega$ .\* This has to be integrated over all elements  $d\omega'$ . Now, with an obvious meaning of  $\psi$ ,

$$\cos \theta' = \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \psi,$$

and if we assume (what will be confirmed by the subsequent calculation) that

$$n = a + b \cos \theta, \quad n' = a + b \cos \theta', \quad . \quad . \quad (79)$$

then

$$\begin{aligned} \frac{h}{\pi} n' e^{-\hbar a^2} d\omega d\omega' &= \frac{h}{\pi} a e^{-\hbar a^2} d\omega d\omega' \\ &\quad + \frac{h}{\pi} b (\cos \theta \cos \alpha + \sin \theta \sin \alpha \cos \psi) e^{-\hbar a^2} d\omega d\omega'. \end{aligned}$$

In order to find the number of particles which after the lapse of the time  $\tau$  lie in  $d\omega$ , this expression is to be integrated over all elements  $d\omega'$  in the neighbourhood of  $d\omega$ . The term with  $\cos \psi$  drops out. Again  $\cos \alpha$  can be replaced by  $1 - \frac{1}{2}a^2$ . We thus have to integrate

$$\frac{h}{\pi} (a + b \cos \theta) e^{-\hbar a^2} d\omega d\omega' - \frac{h}{2\pi} b \cos \theta a^2 e^{-\hbar a^2} d\omega d\omega',$$

where we can put  $d\omega' = 2\pi a da$ . Integrating over  $a$  we find

$$\left( a + b \cos \theta - \frac{b}{2h} \cos \theta \right) d\omega.$$

Thus, the change of the number of particles within  $d\omega$  due to diffusion is

$$-\frac{b}{2h} \cos \theta d\omega. \quad . \quad . \quad . \quad (80)$$

4. The electric force  $E$  which has the direction  $OP$  gives rise to a couple of moment

$$Em \sin \theta$$

which tends to place the particle in the direction  $OP$ . The particle thus acquires the angular velocity

$$\frac{Em \sin \theta}{w},$$

where  $w$  is a coefficient of resistance. We can say also that the points on the unit sphere which represent the particles move with this velocity towards  $P$ . Now, consider a circle with centre  $P$

\* Since  $2\pi A \int_0^\infty e^{-\hbar a^2} a da = 1$ , or  $2\pi A / 2h = 1$ , we have  $A = h/\pi$ .



and spherical radius  $\theta$ . This will be crossed during the time  $\tau$  by all particles whose initial distance from  $P$  was

$$\theta + \frac{Em \sin \theta}{w} \tau,$$

i.e. by the particles whose representative points originally lay within the element

$$\frac{2\pi Em \sin^2 \theta}{w} \tau$$

of the sphere. The number of these particles is

$$\frac{2\pi a Em \sin^2 \theta}{w} \tau.$$

This then is the increase of the number of particles within the circle  $\theta$ . The number of particles between  $\theta$  and  $\theta + d\theta$  increases, therefore, by

$$\frac{4\pi a Em \sin \theta \cos \theta}{w} \tau d\theta,$$

and that within  $d\omega$  by

$$\frac{2a Em \tau}{w} \cos \theta d\omega. \quad . \quad . \quad . \quad (81)$$

Let the state be stationary. Then

$$-\frac{b}{2h} \cos \theta d\omega + \frac{2a Em \tau}{w} \cos \theta d\omega = 0. \quad . \quad . \quad (82)$$

But we know that in this case

$$n = Ce^{\frac{Em \cos \theta}{kT}} \div C \left( 1 + \frac{Em \cos \theta}{kT} \right)$$

which, compared with (79), gives

$$b = \frac{Em}{kT} a.$$

Thus the condition (82) becomes

$$-\frac{Em}{2hkT} a + \frac{2a Em \tau}{w} = 0$$

whence follows

$$h = \frac{w}{4kT\tau}. \quad . \quad . \quad . \quad (83)$$

5. Let now the electric force be given by

$$E = pe^{int}.$$

Then the increase of the number of particles in  $d\omega$  due to the action of this force will be, by (81),

$$\frac{2am\tau}{w} \cos \theta p e^{int} d\omega,$$

and the change of that number due to diffusion, by (80) and (83),

$$-\frac{b}{2h} \cos \theta d\omega = -\frac{2kT\tau}{w} b \cos \theta d\omega,$$

while the total change can be written

$$\frac{\partial b}{\partial t} \tau \cos \theta d\omega.$$

Thus,

$$\frac{\partial b}{\partial t} = \frac{2am}{w} p e^{int} - \frac{2kT}{w} b,$$

whence

$$b = \frac{2amp}{2kT + inw} e^{int}.$$

This enables us to calculate the electric moment prevailing at any instant. If this be denoted, per unit volume, by  $P$ , we have

$$P = \int (a + b \cos \theta) m \cos \theta d\omega = bm \int \cos^2 \theta d\omega = \frac{4}{3} \pi b m,$$

$$i.e. \quad P = \frac{4}{3} \pi m \cdot \frac{2amp}{2kT + inw} e^{int} = spe^{int}, \text{ say.}$$

But we must still take into account that if the electric force, as it occurs in Maxwell's equations, is  $qe^{int}$ , the actual force is found by adding  $\frac{1}{3}P$ . Thus,

$$p = q + \frac{1}{3}sp, \quad p = \frac{q}{1 - \frac{1}{3}s},$$

and

$$P = \frac{s}{1 - \frac{1}{3}s} q e^{int}.$$

This gives the dielectric displacement

$$D = E + P = \frac{1 + \frac{2}{3}s}{1 - \frac{1}{3}s} q e^{int} = \frac{3 + 2s}{3 - s} E. \quad . \quad . \quad (84)$$

Now, let

$$E = ae^{in\left[t - (\mu) \frac{x}{c}\right]}. \quad . \quad . \quad . \quad (85)$$

Then, by the fundamental equations of electrical theory,

$$(\mu)^2 = \frac{3+2s}{3-s}. \quad (86)$$

If we still assume the presence of quasi-elastically bound ions or electrons, another term  $s'$  which we can consider as constant has to be added to the expression for  $s$ . Thus

$$s = \frac{8}{3} \pi a m^2 \cdot \frac{1}{2kT + i n w} + s',$$

which we will write briefly

$$s = \frac{1}{aT + i\beta n} + s'. \quad (87)$$

This is, owing to the resistance  $w$ , a complex expression, so that also the value of  $(\mu)$  determined by (86) is complex. Hence, the wave propagation represented by (85) will be associated with an absorption. The latter, as well as the velocity of propagation or the refractive index, can be derived from (86). In fact, if we put  $(\mu) = \mu(1 - i\kappa)$ , then

$$E = ae^{in\left(t - \frac{\mu}{c}x + i\frac{\mu}{c}\kappa x\right)},$$

and taking the real part,

$$E = ae^{-\kappa \frac{\mu}{c} nx} \cos n\left(t - \frac{\mu x}{c}\right).$$

Thus  $\mu$  is the refractive index, while  $\kappa$  determines the absorption.

It is worthy of notice that the expression (87) becomes real for  $n = \infty$  as well as for  $n = 0$ , and that the values of  $\mu$  and  $\kappa$  for any frequency  $n$  can be expressed in terms of  $s_\infty$  and  $s_0$ . If we denote the "dielectric constant"  $\frac{3+2s}{3-s}$  (cf. (84)) by  $\epsilon$ , then the refractive index for very rapid vibrations will be given by

$$(\mu)^2 = \epsilon_\infty = \frac{3+2s_\infty}{3-s_\infty},$$

whence

$$s_\infty = s' = \frac{3(\epsilon_\infty - 1)}{\epsilon_\infty + 2}. \quad (88)$$

On the other hand, we have for very slow vibrations

$$(\mu)^2 = \epsilon_0 = \frac{3+2s_0}{3-s_0},$$

where

$$s_0 = 3 \frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{1}{\alpha T} + s'.$$

Thus, by (88),

$$\frac{1}{\alpha T} = 3 \left( \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right).$$

Now, for any frequency  $n$ , by (87),

$$s = \frac{1}{\alpha T} \cdot \frac{1}{1 + i \frac{\beta n}{\alpha T}} + s'.$$

Putting for brevity

$$\frac{\epsilon - 1}{\epsilon + 2} = \phi.$$

we substitute here

$$\frac{1}{\alpha T} = 3(\phi_0 - \phi_\infty), \quad s' = 3\phi_\infty.$$

This gives

$$s = 3 \left\{ (\phi_0 - \phi_\infty) \cdot \frac{1}{1 + i \frac{\beta n}{\alpha T}} + \phi_\infty \right\},$$

so that, ultimately,

$$(\mu)^2 = \frac{3 + 2s}{3 - s} = \frac{(2\phi_0 + 1) + (2\phi_\infty + 1)i \frac{\beta n}{\alpha T}}{1 - \phi_0 + (1 - \phi_\infty)i \frac{\beta n}{\alpha T}},$$

*i.e.*

$$(\mu)^2 = \frac{\frac{\epsilon_0}{\epsilon_0 + 2} + i \frac{\beta n}{\alpha T} \cdot \frac{\epsilon_\infty}{\epsilon_\infty + 2}}{\frac{1}{\epsilon_0 + 2} + i \frac{\beta n}{\alpha T} \cdot \frac{1}{\epsilon_\infty + 2}},$$

whence  $\mu$  and  $\kappa$  can be calculated.

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